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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Production of White Light by Mixing the Colours of the Spectrum. By Stroumbo (*Compt. rend.*, **103**, 737—738).—The spectrum is produced by means of a prism which is arranged so that it can rotate about an axis parallel with its faces. When the prism is made to rotate with sufficient rapidity, the spectrum is replaced by a band of white light. The extreme red of the spectrum, however, always remains coloured, because whilst all the other colours pass their position of minimum deviation, the red, which is the least refrangible, does not become mixed with any other colours. It is advisable to intercept this portion of the spectrum by means of a small screen. C. H. B.

Spectra of the Methyl-derivatives of Hydroxyanthraquinone. By C. Liebermann and S. v. Kostanecki (*Ber.*, **19**, 2327—2332).—The compounds are best examined in solution in pure concentrated sulphuric acid. The eight known dihydroxyanthraquinones can be distinguished from one another by the spectra of their sulphuric acid solutions.

The methyl homologues have almost exactly the same properties as the original substances, and as this analogy extends to the spectra it is often possible to determine the constitution with very small amounts of substances. The difference in the spectra caused by the substitution of one methyl-group is extremely small, but this difference increases visibly with the number of methyl-groups.

The relation of chrysophanic acid to chrysazine, previously suggested (*Annalen*, **183**) on the strength of their similar chemical properties, is supported in a striking manner by the spectra of the two compounds.

A table of spectra of methyl homologues and the compounds from

which they are derived, and tables showing the relation of the trihydroxyanthraquinones to each other and to their methyl-derivatives, are given (compare also Krüss, Abstr., 1885, 949).

N. H. M.

Preparation of Calcium Sulphide with a Violet Phosphorescence. By A. Verneuil (*Compt. rend.*, **103**, 600—603).—20 grams of finely powdered calcium oxide prepared by heating the very dense shell of *Hypopus vulgaris*, is intimately mixed with 6 grams of sulphur and 2 grams of starch; and 8 c.c. of a solution of 0·5 gram of basic bismuth nitrate and 100 c.c. of absolute alcohol acidified with a few drops of hydrochloric acid, are added. The mixture is exposed to the air until the greater part of the alcohol has evaporated, and is then heated in a covered crucible at a cherry-red heat for 20 minutes. When completely cooled, the upper layer of calcium sulphate is removed, and the calcined mass powdered and again heated at the same temperature for 15 minutes. If the temperature has not risen too high, the product is granular and friable; if powdered a second time, the brilliancy of the phosphorescence is considerably diminished. The violet colour of the phosphorescence is due to the presence of the small quantity of bismuth.

The phosphorescence of calcium sulphide is not materially increased by the presence of 0·1 per cent. of the sulphides of antimony, cadmium, mercury, tin, copper, lead, uranium, platinum, zinc, or molybdenum, but these substances impart a bluish-green or yellowish-green tinge to the phosphorescence. Sulphides of cobalt, nickel, iron, and silver diminish the phosphorescence, whilst manganese produces the orange shade observed by Becquerel.

A mixture of calcium oxide 100 parts, sulphur 30 parts, starch 10 parts, and lead acetate 0·035 part, yields a sulphide with a beautiful yellowish-green phosphorescence, but if the proportion of lead acetate is increased to 0·4 part, the green colour disappears and the phosphorescence becomes yellowish-white, and diminishes considerably in intensity. With 1·6 part of lead acetate, the yellow tint is more marked, and with 3·5 parts the phosphorescence is orange-yellow. With a greater proportion of the lead salt, the product has a greyish tint and does not phosphoresce at all.

Calcium sulphide obtained by reducing the pure sulphate in a current of hydrogen or carbonic oxide, shows no phosphorescence, and that prepared by heating the sulphate with starch shows only very slight phosphorescence; hence it would seem that pure calcium sulphide is not phosphorescent, and that the phenomenon is due to the presence of small quantities of silica, magnesium, phosphates, and alkalis derived from the shells from which the lime is prepared.

As a general rule, substances which cause the calcium sulphide to frit slightly when heated, increase the brilliancy of the phosphorescence.

The product obtained by heating a mixture of strontium carbonate 100 parts, sulphur 30 parts, and arsenious oxide 5 parts, shows a greenish-blue phosphorescence if the strontium carbonate has been prepared from the chloride and ammonium carbonate, but the phosphorescence is greenish-yellow if the strontium carbonate has

been precipitated by means of sodium carbonate. The difference is due to the retention of a small quantity of alkali by the strontium carbonate. C. H. B.

Fluorescence of Manganese Compounds in a Vacuum under the Influence of the Silent Discharge. By L. De Boisbaudran (*Compt. rend.*, **103**, 468—471).—All the sulphates used in these experiments were heated to dull redness, and the carbonates and oxides were strongly heated.

Manganese sulphate alone, and trimanganese tetroxide prepared from the carbonate, show no fluorescence.

Calcium sulphate alone gives a feeble fluorescence with a continuous spectrum, but if it contains a trace of manganese sulphate it gives a brilliant green fluorescence, the spectrum of which consists of a broad band which begins at about 6600, attains its maximum intensity at about 5400, and fades away between the blue and the violet.

Calcium carbonate alone shows a feeble fluorescence, but if mixed with a small quantity of manganese, it shows a brilliant orange-yellow fluorescence characterised by a band which begins about 6700, attains its maximum intensity at about 5890, and fades away at 5260. This fluorescence is much more strongly marked than that observed with the sulphates.

Magnesium sulphate alone gives a faint greenish fluorescence, but if mixed with manganese sulphate it gives a brilliant red fluorescence characterised by a band which begins nebulously at about 6720, attains its maximum at 6200, and fades away at about 5540.

Magnesium carbonate mixed with manganese shows the same fluorescence as the sulphates.

Zinc sulphate alone shows a feeble rose-coloured fluorescence, but if mixed with manganese sulphate it shows an orange-red fluorescence, which is characterised by a band which begins nebulously at 6720, attains a maximum at about 6280, and fades away near 5380.

Cadmium oxide alone or mixed with manganese oxide gives no fluorescence. Cadmium sulphate alone shows only a feeble pale greenish-yellow fluorescence, but if it is mixed with manganese sulphate it gives a very brilliant yellowish-green fluorescence, the spectrum of which consists of a broad band which begins at 6620, attains its maximum at 5590, and fades away at about 4560. This is the most brilliant of all the manganese fluorescences.

Strontium sulphate alone shows a pale lilac fluorescence with a continuous spectrum, and the carbonate or oxalate after being strongly heated shows a blue fluorescence. These fluorescences are not materially affected by the presence of manganese.

Lead sulphate alone gives a feeble violet fluorescence, but if mixed with manganese sulphate it gives a beautiful yellow fluorescence characterised by a band which begins at about 6560, attains its maximum at 5820—5760, and ends at 5310—5260. Lead oxide, whether pure or mixed with manganese, gives no notable fluorescence.

Beryllium sulphate alone gives a somewhat marked green fluorescence, but if it is mixed with a trace of manganese sulphate the fluorescence is stronger and is yellowish-green. It gives a spectrum

consisting of a fairly brilliant band which begins at 6690, attains a maximum at 5640, and fades away at 4840—4800. An excess of beryllium sulphate prevents the development of the manganese fluorescence.

The character of the fluorescence and the position and character of the bands in its spectrum vary with the nature of the substance with which the manganese is mixed. These fluorescences constitute an extremely delicate test for manganese. C. H. B.

Fluorescence of Bismuth Compounds. By L. De Boisbaudran (*Compt. rend.*, **103**, 629—631).—Bismuth sulphate alone, previously heated to dull redness, shows no fluorescence when subjected to the action of the silent electrical discharge in a vacuum, but the admixture of small quantities of this salt with various other sulphates confers upon them the power of fluorescing under these conditions. In all cases, the sulphates were previously heated to dull redness. If the proportion of bismuth is gradually increased, the fluorescence at first increases in brilliancy, attains a maximum, then becomes weaker, and finally disappears even whilst the proportion of bismuth is still very small.

With calcium sulphate, the fluorescence is orange-red, and its spectrum consists of a band which begins very nebulously at 6730, attains its maximum intensity at 6140, and fades away gradually at about 5780. With strontium sulphate, the fluorescence is orange, and is more brilliant than with the calcium salt. Its spectrum consists of a band which begins very nebulously at 6640, attains its maximum intensity at 5980, and fades away at about 5637. With barium sulphate, the fluorescence is redder than with calcium sulphate, and is characterised by a band which begins nebulously at 6540, attains its maximum intensity at about 6220, and fades away gradually at 5840—5850. With magnesium sulphate, the fluorescence is still redder but is not so brilliant as in the preceding cases. It is characterised by a band which begins nebulously at 6750—6760, attains its maximum intensity at 6320—6330, and fades gradually away at about 5860. The fluorescence of the corresponding oxides is not appreciably affected by the presence of bismuth oxide. No fluorescence was observed with zinc, cadmium, and lead sulphates, or zinc and cadmium oxides, in the presence of bismuth.

The spectrum of this fluorescence is a more delicate test for bismuth than the spark spectrum. C. H. B.

Electrical Conductivity of Gases and Vapours. By J. Luvini (*Compt. rend.*, **103**, 495—497).—The author's experiments, combined with those of previous investigators, show that gases and vapours at any temperature or pressure are perfect insulators, and cannot be electrified by internal friction or friction with solids and liquids. Measurements were made by observing the divergence between a pith ball suspended by cocoon silk and a brass sphere suspended in the same way in an atmosphere of the gas to be examined, both sphere and pith ball being electrified. The gases used were air saturated with moisture at various temperatures between

16° and 100°, moist hydrogen, moist carbonic anhydride, mercury vapour at 100°, vapour of ammonium chloride, air heated by burning charcoal and by a candle flame, smoke from a smouldering candle-wick, vapours from burnt sugar, incense, &c.

The belief that gases at very low pressures or high temperatures are conductors arises from a confusion between resistance to a *disruptive* discharge and resistance to a *conductive* discharge.

All theories in which gases and vapours are regarded as conductors or capable of being electrified by friction must be abandoned.

C. H. B.

Relation of the Conductive Capacity of Gases to their Temperature. By A. Winkelmann (*Ann. Phys. Chem.* [2], **29**, 68—113).—In these experiments, the conductive capacity is determined by means of three horizontal copper plates immersed in the gas and separated from one another by glass balls, the upper and lower plates being maintained at fixed and different temperatures. The temperature of each plate was indicated by a delicate thermometer.

The results obtained are—

For air, mean of four experiments	0·00206.
,, carbonic anhydride, four experiments.....	0·00366.
,, hydrogen, two experiments	0·00206.

The heat given off by a plate immersed in a gas is different according to its orientation, hence that given off by a given area cannot be determined from the rate of cooling of the whole. H. K. T.

Electrical Conductivity of Solid Substances at a High Pressure. By L. Graetz (*Ann. Phys. Chem.* [2], **29**, 314—330).—Hitherto our knowledge of the conductivity of electrolytes is derived for the most part from results obtained with the substances in the dissolved and not in the fused condition. Although it is *à priori* to be expected that the law governing these phenomena in the case of a homogeneous media would be of a simpler character than those in the case of heterogeneous media, namely, a solution of salt in water, yet the result of experience is the reverse.

The only generalisation at present deduced is that solid substances are not conductors at low temperatures, but their conductivity commences at temperatures far below the melting point, and increases with the temperature.

If then this increase of conductivity is due to an increase of molecular mobility and of the number of molecular impacts, increase of pressure without alteration of temperature should be effective to a like degree. In the paper, this point is examined by means of a compression apparatus, capable of giving a pressure of upwards of 4000 atmospheres. The results are given for the halogen-compounds of lead and silver, and for sodium nitrate. The substances examined are divisible into two classes, in the one of which, with application of maximum pressure, the resistance rapidly decreases to a constant point, and in the other this minimum resistance is, under the same condition, only attained after several hours. To the former class

belong the halogen-compounds of silver, to the latter those of lead and sodium nitrate. In the paper full details are given of the apparatus used, and of the methods of experiments; the results are tabulated. V. H. V.

Specific Heats of Homologous Series of Liquid Organic Compounds. By R. Schiff (*Annalen*, **234**, 300—337).—The author has determined the specific heats of a large number of hydrocarbons, acids, alcohols, and ethereal salts, at different temperatures, and has arrived at the following results. All the ethereal salts of fatty acids of the formula $C_nH_{2n}O_2$, have the same specific heat at the same temperature.

The specific heat of these substances at t is represented by the equation $Kt = 0{\cdot}4416 + 0{\cdot}00088t$, and the mean specific heat between t and t' by $Ct - t' = 0{\cdot}4416 + 0{\cdot}00044(t + t')$.

	$Kt =$
For methyl benzoate	$0{\cdot}363 + 0{\cdot}000750t$.
,, ethyl benzoate	$0{\cdot}374 + 0{\cdot}000750t$.
,, propyl benzoate	$0{\cdot}383 + 0{\cdot}000750t$.
Methyl phenoxide and creso-oxide	$0{\cdot}4054 + 0{\cdot}00086t$.
,, xylenoxide	$0{\cdot}4170 + 0{\cdot}00086t$.
Ethyl and propyl phenoxide, ,, creso-oxide	$0{\cdot}4288 + 0{\cdot}00086t$.
Benzene, toluene, meta- and para-xylene	$0{\cdot}3834 + 0{\cdot}001043t$.
Ethylbenzene, pseudocumene, mesitylene	$0{\cdot}3929 + 0{\cdot}001043t$.
Propylbenzene, cymene	$0{\cdot}400 + 0{\cdot}001043t$.
Acetic acid, Propionic acid, Butyric acid	$0{\cdot}440 + 0{\cdot}001418t$.
Isobutyric acid, Valeric acid	$0{\cdot}4352 + 0{\cdot}001418t$.
Formic acid	$0{\cdot}4966 + 0{\cdot}000709t$.

Pawlewsky (Abstr., 1883, 276) has pointed out that the critical temperature of the ethereal salts of the fatty acids is 182° higher than their boiling point.

The author divides the distance between the absolute zero and the critical temperature of an ethereal salt into 100 equal parts, which he terms critical degrees.

In the table (p. 7) LX cr represents 60 of these critical degrees; K_{LX} the true specific heat at this temperature; D_{LX} the sp. gr. at this temperature, and KD_{LX} the product of these two values.

Equal volumes of these substances have the same specific heat at the same "critical degree."

The author disputes the accuracy of the conclusions which De Heen (*Physique comparée*, 39) draws from his researches on this subject, and he also criticises the results obtained by v. Reis.

	LX cr.	K_{LX}.	D_{LX}.	KD_{LX}.
Ethyl acetate	46·2	0·4822	0·8671	0·418
Propyl formate	48·6	0·4844	0·8629	0·418
Methyl propionate	47·9	0·4837	0·8801	0·425
Isobutyl formate	58·2	0·4928	0·8449	0·416
Propyl acetate	61·6	0·4958	0·8420	0·417
Ethyl propionate	59·6	0·4940	0·8455	0·417
Methyl isobutyrate	56·1	0·4910	0·8487	0·417
Methyl butyrate	61·5	0·4957	0·8544	0·423
Isoamyl formate	74·4	0·5070	0·8223	0·417
Isobutyl acetate	70·2	0·5034	0·8195	0·412
Propyl propionate	73·8	0·5065	0·8266	0·418
Ethyl butyrate	71·4	0·5044	0·8256	0·415
„ isobutyrate	66·0	0·4997	0·8214	0·410
Methyl valerate	69·6	0·5028	0·8291	0·416
Isoamyl acetate	85·2	0·5165	0·8047	0·415
Isobutyl propionate	82·2	0·5139	0·8059	0·414
Propyl butyrate	86·4	0·5177	0·8050	0·416
„ isobutyrate	81·0	0·5129	0·8047	0·413
Ethyl valerate	80·7	0·5126	0·8066	0·413
Amyl propionate	97·2	0·5271	0·7979	0·420
Isobutyl butyrate	94·5	0·5247	0·7891	0·413
„ isobutyrate	89·1	0·5200	0·7908	0·411
Propyl valerate	93·3	0·5237	0·7943	0·416
Isoamyl butyrate	107·1	0·5358	0·7841	0·420
„ isobutyrate	100·5	0·5300	0·7806	0·413
Isobutyl valerate	102·0	0·5313	0·7775	0·413
Isoamyl valerate	112·5	0·5406	0·7794	0·421

W. C. W.

Saturation of Normal Arsenic Acid with Barium Hydroxide. By C. Blarez (*Compt. rend.*, **103**, 746).—The developments of heat accompanying the addition of successive equivalents of barium hydroxide to a dilute solution of arsenic acid are given in the following table:—

1st	equivalent	develops	+ 14·00
2nd	„	„	+ 27·75
3rd	„	„	+ 43·25
4th	„	„	+ 43·50
5th	„	„	+ 44·00

The phenomena are not similar to those observed when arsenic acid is neutralised by alkalis, lime, or strontia. Cochineal and helianthin change when the first function of the acid is somewhat more than neutralised, but phenolphthaleïn indicates accurately the neutralisation of the second acid function. Even in presence of four or five equivalents of baryta, the precipitate is tribarium arsenate, a result different from that obtained when arsenic acid is neutralised with lime or strontia, or when orthophosphoric acid is neutralised with baryta. C. H. B.

Saturation of Arsenic Acid with Calcium and Strontium Oxides. By C. Blarez (*Compt. rend.*, **103**, 639—640).—The heat developed by the saturation of a normal solution of arsenic acid by means of calcium or strontium oxide in aqueous solution is given in the following table :—

	Calcium oxide.	Strontium oxide.
First equivalent	14·5	14·17
Second equivalent	12·5	12·33
Third „	2·52	3·88
Fourth „	0·28	1·03
Fifth „	0·25	—

Neutralisation with the first equivalent is distinctly indicated by cochineal, but less distinctly by methyl-orange, and neutralisation with the second equivalent is indicated fairly well by phenolphthaleïn. The arsenate precipitated on addition of three equivalents of base is somewhat variable in composition, but approximates to the tribasic salt. With four and five equivalents, the precipitated arsenate is somewhat basic. The much greater tendency of calcium and strontium arsenates to dissociate in presence of water, distinguishes them from the corresponding phosphates. C. H. B.

Sodium Glycerolate. By de Forcrand (*Compt. rend.*, **103**, 596—599).—Sodium glycerolate, $C_3H_7NaO_3$, was prepared by Lett's method (*Ber.*, **5**, 159). Heat of solution at 16°, $C_3H_7NaO_3,C_2H_6O$, − 1·08 cal.; $C_3H_7NaO_3$, + 1·07. From these values, and the heat of solution and neutralisation of glycerol, and the heat of solution of alcohol as determined by Berthelot, it follows that—

$C_3H_5(OH)_3$ liq. + NaHO solid + C_2H_6O liq. = H_2O solid + $C_3H_7NaO_3$ solid ..... develops + 16·60 cal.

$C_3H_8O_3$ liq. + NaHO solid = $C_3H_7NaO_3$ solid + H_2O solid ..... „ + 12·02 „

and hence—

$C_3H_7NaO_3$ solid + C_2H_6O liq. = $C_3H_7NaO_3,C_2H_6O$ solid ..... „ + 4·58 „

This result confirms the view that the substitution of sodium takes place in the glycerol and not in the ethyl alcohol.

$C_3H_8O_3$ liq. + Na solid = $C_3H_7NaO_3$ solid + H gas ..... develops + 43·89 cal.

$2C_3H_8O_3$ + Na_2O solid = $2C_3H_7NaO_3$ solid + H_2O solid ..... „ + 29·02 × 2 „

and lastly—

$C_3H_8O_3$ liq. + C_2H_5NaO diss. in nC_3H_6O liq. = $C_3H_7NaO_3,C_2H_6O$ solid, ppt. in nC_2H_6O liq. „ + 3·92 „

This result shows that the formation of $C_3H_7NaO_3,C_2H_6O$ is

exothermic, whilst the precipitation of $C_3H_7NaO_3$ alone would be endothermic.

The alkaline glycerolates possess a somewhat general property of uniting with one molecule of monohydric alcohols to form crystallisable compounds. The thermochemical data show that polyhydric alcohols yield more stable derivatives than monohydric alcohols.

C. H. B.

Heat of Evaporation of Homologous Carbon-compounds. By R. Schiff (*Annalen*, **234**, 338—350).—The author uses an apparatus partly constructed of silver, which is so arranged as to prevent the vapour of the boiling liquid being superheated, and also to ensure the dryness of the vapour before it enters the calorimeter, two points to which sufficient attention has not been directed in the different forms of apparatus used by Berthelot (*Mécanique Chimique*, **1**, 289), Brix (*Ann. Chim. Phys.*, **55**), and Depretz (*Ann. Chim. Phys.*, **24**, 323).

The author's tabulated results show that the heat of evaporation decreases as the molecular weight increases. In the case of isomerides, the substance with the lowest boiling point has the lowest heat of evaporation. The results confirm Trouton's statement that the molecular heats of evaporation are proportional to the absolute temperature at which the evaporation takes place (*Phil. Mag.* [5], **18**, 84). The coefficient of expansion at 0° is inversely proportional to the absolute temperature of the boiling point under the normal pressure.

W. C. W.

Development of Heat when Powders are Moistened. By F. Meissner (*Ann. Phys. Chem.* [2], **29**, 114—131).—The author uses two experimental methods, a thermometric and a calorimetric. In the first, weighed quantities of the carefully dried powder and of water are brought together in a small glass vessel, their temperature having been carefully noted before mixing. The rise in temperature produced is recorded from time to time by a delicate thermometer immersed in the mixture. The second set of experiments were conducted in a Bunsen's calorimeter. The substances experimented on were ignited silica, "magnesia alba," glass powder, emery and animal charcoal with water, benzene, amyl alcohol, and glycerol.

For water and silica, the author finds a rise in temperature of 3·8—4·5° C., with initial temperatures ranging from 0—19°; this result is contrary to that of Jungk (*Ann. Phys. Chem.*, 125, 292), who states that with initial temperatures below 4° there is absorption of heat.

The author considers that the development of heat is due to the expansion of the colloïd when moistened, or that potential molecular energy is converted into heat.

H. K. T.

Determination of the Specific Gravity of Soluble Substances. By L. Zehnder (*Ann. Phys. Chem.* [2], **29**, 249—263).—In this paper, a simple method for the determination of the specific gravity of soluble substances is described, by means of which results accurate to the one-thousandth part can be readily obtained. The principle of it is as follows:—The substance to be determined is weighed

in the pyknometer, and the latter is then placed in an inverted position under water, so that the solid substance falls out, the air from the pyknometer being at the same time collected by a funnel provided with a bent tube, and completely filled with water; from this funnel the air is retransferred to the pyknometer, which is then again weighed; thus is obtained the weight of a volume of water equal to that occupied by the weight of the substance taken, which relation gives directly the specific gravity. To collect the displaced air, the pyknometer is inverted under a funnel provided with a delivery-tube, twice bent, and ending in a capillary opening, by means of which the air is again decanted into the pyknometer.

This method requires the following determinations: the weight of the substance whose sp. gr. is to be determined, the weight of the water replaced by it, and the capacity of the pyknometer; the difference between them is the volume of air; this is corrected for differences of temperature and pressure during the determination, and the corrected volume of air subtracted from the capacity of the pyknometer gives the corrected volume occupied by the substance; on dividing the weight of the substance by the latter value, the specific gravity is obtained. The special precautions to be adopted are discussed in full, and determinations are given of common salt and sugar candy, the results of which are fairly satisfactory. V. H. V.

Tension of Dissociation of Ammonium Hydrogen Carbonate. By Berthelot and André (*Compt. rend.*, **103**, 665—671).—The decomposition of ammonium hydrogen carbonate by water increases only very slightly with an increase in the proportion of water, and the maximum change is not effected until after a considerable lapse of time. The heat of dissolution of 1 gram-mol. in 25 litres of water is — 6·85 cal.; whilst the heat of dissolution in 6—8 litres is — 6·2 cal.

Perfectly dry ammonium hydrogen carbonate has no sensible tension of dissociation at ordinary temperatures in presence of air, ammonia, or carbonic anhydride, under a pressure of two-thirds of an atmosphere. Even when a current of these gases is passed over the salt, the evidence of any dissociation is extremely slight. That the salt does, however, possess a distinct, though extremely small, vapour-tension, is shown by the fact that if it is left in a closed space over sulphuric acid, the latter increases in weight, and crystals of ammonium hydrogen sulphate form on the edge of the dish containing it.

These results are materially affected by the presence of very small quantities of water. If the water is entirely in the state of vapour, it exerts but little influence on the vapour-tension of the salt, but the effect is much greater in presence of liquid water, and if the salt is placed in a closed space in which there is also a vessel containing water, the latter increases in weight owing to absorption of ammonia.

The three constituents of the salt do not play the same part in its dissociation. Carbonic anhydride and ammonia are without influence on its vapour-tension at the ordinary temperature, whilst water determines its decomposition independently of the ordinary laws of dissociation. C. H. B.

Decomposition of Ammonium Hydrogen Carbonate by Water and Diffusion of the Ammonia through the Atmosphere. By BERTHELOT and ANDRÉ (*Compt. rend.*, **103**, 716—721).—A concentrated solution of ammonium carbonate, containing ammona and carbonic anhydride in the ratio 1 : 1·85, was placed in a closed space, which also contained a vessel with a known weight of water. The atmosphere contained carbonic anhydride, but no appreciable quantity of ammonia. At first, the quantity of carbonic anhydride absorbed by the water in the second vessel was relatively greater than the quantity of ammonia, but after about eight days the distribution of ammonia and carbonic anhydride was uniform in both vessels. Similar results were obtained with dilute solutions, and it follows that pure water, in an atmosphere containing a small quantity of ammonia and a relatively much larger quantity of carbonic anhydride, tends to reform the acid carbonate, a result probably due to the fact that the carbonic anhydride, by reason of its greater insolubility, maintains a higher tension in the atmosphere. The diffusion of ammonia from water to air in presence of carbonic anhydride does not take place in accordance with the same laws as the diffusion in the absence of any gas which can combine with the ammonia. The rate of diffusion of free ammonia from its aqueous solution into the air is very much more rapid than the diffusion of ammonia in combination with carbonic acid. The diffusion of free ammonia is accelerated by the presence of sulphuric acid, which absorbs the alkali from the atmosphere, but the presence of this acid has very little effect on the diffusion of ammonia from a solution of the carbonate, and the effect is less the more dilute the solution.

In presence of an excess of carbonic anhydride, the transference of ammonia through the atmosphere to an aqueous liquid takes place in a manner entirely different from the similar transference of ammonia in presence of an inert gas. The latter is conditioned by the tension of the ammonia in the solutions, whilst the former depends on the relative tensions of the carbonic anhydride in the liquids and the surrounding atmosphere. It is, in fact, the diffusion of the carbonic anhydride which regulates the decomposition of the ammonium hydrogen carbonate and the transference of the ammonia through the atmosphere. C. H. B.

Inorganic Chemistry.

Conversion of Calcium Hypochlorite into Calcium Chlorate. By G. LUNGE (*J. Soc. Chem. Ind.*, **4**, 722—724).—It has already been shown by the author that the reaction $6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2$ does not take place completely and without considerable loss of oxygen, except in presence of an excess of chlorine, although that chlorine does not appear in the equation. The author's experiments point to the following conclusions:—The most

favourable way of converting hypochlorite into chlorate is to raise the temperature of the solution, and simultaneously have an excess of chlorine present therein. A large excess of chlorine is useless, perhaps injurious, for the yield of chlorate. On the large scale, it is not necessary to raise the temperature by artificial means, the heat produced by the reaction being sufficient to complete it. The conversion at the ordinary temperature proceeds almost at once to the limit of about 70 per cent., but subsequently makes very slow progress, so that it is impracticable to wait for its completion without heating. D. B.

A Crystalline Silico-carbonate from Soda Liquors. By C. Rammelsberg (*Chem. Ind.*, **9**, 110—111).—Two specimens of crystals removed from the pump of a carbonating tower at the "Hermannia" Chemical Works at Schönebeck had the following composition:—

	CO_2.	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.
I.	22·75	14·99	7·38	13·28	22·37	19·23 = 100
II.	21·50	15·00	8·03	12·41	21·66	21·40 = 100

Allowing for adhering soda liquor, these numbers lead to the formula $Na_{18}Ca_6Al_2(Si,C)_{21}O_{63} + 30H_2O$, or the substance is a compound of the isomorphous normal carbonates and silicates

$$3[3Na_2(Si,C)O_3,2Ca(Si,C)O_3],2Al(Si,C)_3O_{18}.$$

The crystals are rhombic, exhibiting the form of the primary pyramid with its acuter terminal edges truncated, or frequently a tabular form due to the development of the end face; the ratio of the axes is 0·5295 : 1 : 1·73.

These crystals were first observed in 1880, but the specimen then analysed contained an admixture of gay-lussite, and the silica and alumina were not recognised as essential constituents. M. J. S.

Sodium-calcium Carbonates from the Soda Manufacture. By C. Reidemeister (*Chem. Ind.*, **9**, 111).—In the *Chemische Industrie* for 1884 the author described the rhombic crystals analysed by Rammelsberg (see preceding Abstract) as a hydrated sodium calcium carbonate. They are now found to occur in both the crude and carbonated liquors. In the former, in which formerly only gay-lussite had been recognised, they have now been observed with crystals of gay-lussite deposited on their surfaces. The gay-lussite crystals are chiefly deposited from liquors in process of cooling; the silico-carbonate from those undergoing slow evaporation. M. J. S.

Double Nitrites of Cæsium and of Rubidium. By T. Rosenbladt (*Ber.*, **19**, 2531—2535).—The double nitrite of cæsium and cobalt, $3CsNO,Co(NO_2)_3 + H_2O$, is formed by boiling equal parts of cobalt nitrate and sodium acetate in water (15 parts), filtering, and adding to the cold solution first acetic acid (20 parts), and then a strong solution of sodium nitrite until the liquid has an orange colour, it is then filtered, and treated with a solution of a

cæsium salt. The double salt $3RbNO_2,Co(NO_2)_3 + H_2O$ is prepared in a similar manner. They are both lemon-coloured crystalline salts, and resemble in their behaviour Fischer's potassium-compound, except in their solubility in water, the cæsium salt dissolving only in 20,100 parts of water at 17°, and the rubidium salt in 19,800 parts of water. The method employed in analysing these compounds is described.

Thallium also yields a double salt with cobalt nitrite; it is a red crystalline compound, soluble in 23,810 parts of water.

N. H. M.

Decomposition of Glass by Carbonic Anhydride condensed on its Surface. By R. Bunsen (*Ann. Phys. Chem.* [2], **29**, 161—165).—Formerly the author attributed the absorption of carbonic anhydride by glass-wool rather to an interpenetration of the glass by the molecules of the liquefied gas rather than to any chemical change (Abstr., 1884, 146). This view would also be confirmed by the observations on the stability of glass towards the most concentrated hydrochloric acid. However, if the glass-wool be damp, whereby the absorption of the gas is remarkably increased (Abstr., 1885, 867), the possibility of a chemical change is not precluded. Accordingly the glass (49·453 grams) used in the experiment was exhausted with water, and a residue obtained from it corresponding to the decomposition of 2·882 grams of glass, or 5·83 per cent. of the whole. Even if the chemical change consists in the production at first of sodium carbonate, which would take up a further quantity of carbonic anhydride, corresponding with the formation of sodium hydrogen carbonate, which on subsequent heating would again be driven off, yet all the carbonic anhydride absorbed cannot be accounted for in this way. The phenomenon is thus not only one of chemical change, but also of absorption, the particular degree of each of which cannot be estimated.

If, then, carbonic acid can decompose glass, the same is to be expected of water. Observations in the course of experiments on the determination of the tension of aqueous vapour at high temperatures are quoted to show that glass tubes containing water-vapour when heated at 88° are converted into a white porcelain-like mass, and that their inner diameter is diminished by one-tenth. V. H. V.

Note.—On the decomposition of glass by carbonic anhydride under high pressures compare Pfaundler (Abstr., 1885, 868). V. H. V.

Purification of Yttria. By L. de Boisbaudran (*Compt. rend.*, **103**, 627—629).—A comparatively very pure sample of yttria was subjected to 32 series of fractionations by means of ammonia. The product of the last precipitation of the thirty-second series showed a less brilliant fluorescence than the original earth, and the bands of $Z\alpha$ and $Z\beta$ in the spectrum had diminished considerably in intensity, whilst the bands of samarium retained their original vigour. The colour of the fluorescence had changed from yellowish-green to orange-yellow.

This last precipitate was submitted to 26 series of fractionations by means of oxalic acid. The brilliancy of the fluorescence continu-

ally diminished, but, contrary to the phenomena observed during the first fractionation, the samarium bands diminished in intensity much more rapidly than the bands of $Z\alpha$ and $Z\beta$. The earth from the oxalate precipitated at the end of the fifth fractionation showed very faintly the citron band and the double green band of $Z\alpha$ and $Z\beta$, with a trace of the red bands of samarium. The oxalate from the twenty-sixth fractionation yielded a very white earth which showed a trace of the citron band of $Z\alpha$, but none of the red, green, blue, and violet bands in the spectrum described by Crookes. This yttria gave no fluorescence when mixed with lime, but its hydrochloric acid solution gave a brilliant spark spectrum of yttrium.

The sulphate prepared from the last precipitate from the fractionation with oxalic acid gave a rose-coloured fluorescence due to the presence of a trace of bismuth. C. H. B.

Heating and Cooling of Cast Steel. By Osmond (*Compt. rend.*, **103**, 743—746).—The phenomena which accompany the heating and cooling of cast steel were investigated by means of a thermo-electric couple connected with an aperiodic galvanometer.

Barrett observed that when a bar of hard iron is cooled from a white heat there is a sudden development of heat at dull redness, and the magnetic properties of the iron change abruptly. He distinguished this phenomenon by the name *recalescence*. Chatelier and Pinchon found that at about 700° a molecular modification of pure iron is formed.

The author's experiments show that as the proportion of carbon increases from 0·16 to 1·25 per cent. the temperature at which the molecular alteration takes place falls, whilst the point of recalescence rises, until in hard steel the two points coincide. The rate at which heating takes place has no influence on the temperature at which the two changes take place, but these temperatures are affected by the rate of cooling, and are lower the greater the rapidity with which cooling takes place. In quick tempering, no such phenomena are observed; the heat corresponding with the non-effected changes remains in the iron. The two critical points also fall somewhat if the initial temperature of heating is raised. During annealing after tempering, the latent heat of tempering is liberated gradually and not abruptly.

C. H. B.

Tungsten. By T. Kniesche (*Chem. Zeit.*, **10**, 1067—1068).—In treating tungsten ores, sodium tungstate is first obtained, then from this tungstic acid, which in its turn is reduced at a temperature of 1600° to metallic tungsten. The preparation of the chemically pure metal is simply a question of time; any way, as obtained at present, it is useful in steel making. It must be added only when the iron is in a perfectly fluid state. Sodium tungstate is used for rendering inflammable materials fireproof. D. A. L.

Titanium. By O. v. Pfordten (*Annalen*, **234**, 257—299).—The sulphides of those metals which have a strong affinity for oxygen cannot be obtained in the pure state by passing carbon bisulphide over the metallic oxides at a red heat, but they can be prepared by the

action of pure sulphuretted hydrogen on the metallic chlorides. The gas must be passed through chromous chloride to remove traces of oxygen, and is then dried by means of phosphoric oxide. The author disputes Thorpe's statement (Trans., 1885, 492) that sulphuretted hydrogen can be dried by passing the gas through sulphuric acid. At the ordinary temperature, sulphuretted hydrogen reduces titanic chloride to titanous chloride; at a higher temperature, a compound is precipitated, which is probably a sulphochloride. Crystals of titanium disulphide, TiS_2, are deposited when sulphuretted hydrogen and the vapour of titanium tetrachloride are passed through a red-hot tube from which atmospheric air has been carefully expelled. The bisulphide is not attacked by hydrogen at a red heat in the presence of an excess of sulphuretted hydrogen. At a red heat, it is oxidised completely by carbonic anhydride, and it splits up into the sesquisulphide, Ti_2S_3, and sulphur in an atmosphere of hydrogen or nitrogen. The sequisulphide is a metallic grey substance, insoluble in sodium hydroxide solution; it dissolves in nitric and strong sulphuric acids with a green coloration. The author is of opinion that the sesquisulphide described by Thorpe (*loc. cit.*) is an impure substance, and that its green colour is due to the presence of vanadium.

The sesquisulphide is reduced to monosulphide by hydrogen at a higher temperature than that at which refractory glass softens. The crystals of the monosulphide are dark red. Dilute nitric acid attacks the monosulphide with difficulty; in other respects, this substance resembles the sesquisulphide. W. C. W.

Atomic Weight of Germanium. By L. de Boisbaudran (*Compt. rend.*, **103**, 452—453).—Winkler's recent determination of the atomic weight of germanium, 72·32 (Abstr., 1886, 985), agrees perfectly with the value calculated by the author from the wave-lengths of the lines in the germanium spectrum (Abstr., 1886, 768). The law of proportionality between the variations in the atomic weights of the elements, and the variations in the wave-lengths of the lines in their respective spectra, thus receives further confirmation. C. H. B.

Gold Oxides. By G. Krüss (*Ber.*, **19**, 2541—2549).—Aurous oxide, Au_2O, could not be obtained in the pure state by any of the known methods. It is prepared by treating the double bromide of gold with aqueous sulphurous acid at 0° until the intense red colour of the bromide has disappeared. The colourless solution of aurous bromide so formed is warmed with potash, which causes a separation of aurous hydroxide. The oxide is dark violet when moist, greyish-violet when dry; when freshly precipitated, it dissolves in cold water, yielding an indigo-coloured solution with a brownish fluorescence; it is insoluble in hot water. The solution has a characteristic absorption spectrum showing a band at $\lambda = 587{\cdot}0$. Hydrochloric and hydrobromic acids convert it into gold and the corresponding auric compounds; other acids have no action. The hydroxide parts with water at 200°, and at 250° gives up its oxygen.

Aurosoauric oxide, Au_2O_2 (compare Schottländer, Abstr., 1883, 853),

is prepared by gradually heating pure auric hydroxide up to 160° until the weight remains constant. It is a fine dark yellowish-brown powder, is very hygroscopic, and can only be kept over phosphoric anhydride. When heated above 173°, it gives off oxygen.

Auric oxide, Au_2O_3, is conveniently obtained by treating auroauric chloride (1 part) with water (50 parts), boiling the solution, and adding finely powdered magnesia alba, stirring the whole time, until the red colour of the auric chloride has disappeared. The gold trihydroxide is filtered, mixed with water (20 parts), treated with nitric acid, sp. gr. 1·4 (10 parts), and left for 24 hours. The residue, after filtering, is mixed with an equal amount of water and nitric acid, and heated for six hours at 100°. The undissolved portion is now free from magnesia, and is washed with water to remove nitric acid. The pure auric hydroxide has a yellowish-brown colour when moist, and is rather readily soluble in nitric acid. When kept for weeks over phosphoric anhydride, it is converted into aurylic hydroxide, AuO·OH, and when carefully heated yields auric oxide.

The so-called "purple oxide of gold" appears to be gold in a finely divided state.

The author was unable to obtain Prat's gold superoxide and Figuier's auric acid (*Compt. rend.*, **70**, 844), or any other oxide of gold than the three described. This behaviour of gold is in accordance with the position (between platinum and mercury) assigned to it in the periodic arrangement of the elements. N. H. M.

Solubility of some Gold Compounds. By T. Rosenbladt (*Ber.*, **19**, 2535—2538).—The following table shows the amounts of the anhydrous double salts contained in 100 parts by weight of aqueous solution at the given temperatures:—

	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.	90°.	100°.
$NaAuCl_4$	58·2	60·2	64·0	69·4	77·5	90·0	—	—	—	—
$LiAuCl_4$	53·1	57·7	62·5	67·3	72·0	76·4	81·0	85·7	—	—
$KAuCl_4$	27·7	38·2	48·7	59·2	70·0	80·2	—	—	—	—
$RbAuCl_4$	4·6	9·0	13·4	17·2	22·2	26·6	31·0	35·3	39·7	44·2
$CsAuCl_4$	0·5	0·8	1·7	3·2	5·4	8·2	12·0	16·3	21·7	27·5

The solubilities of the double salts (with exception of the lithium salt) are inversely proportional to the molecular weights of the salts. N. H. M.

Mineralogical Chemistry.

Artificial Breithauptite from the Mechernich Lead Furnaces. By A. Brand (*Zeit. Kryst. Min.*, **12**, 234—239).—In 1885 the author found a number of peculiar crystals in the clay used for stopping the tap-holes of the lead furnaces in which antimonial lead was smelted. They occur in all the furnaces; the clay being pulverised and used again. It is therefore impossible to determine whether they were originally formed in the smelting of hard lead. The crystals were columnar, hexagonal prisms, 0·1 to 0·5 mm. thick, and 5 to 26 mm. long. They were brittle, had an uneven fracture, adamantine lustre, steel-grey to copper-red colour, and greyish-brown streak. The hardness was 5 to 5·5, and the sp. gr. about 8. Analysis of carefully purified material gave the following results:—

Sb.	Ni.	Co.	Pb.	Cu.	Fe.	Total.
65·46	29·67	1·12	1·39	0·16	1·45	99·25

The formula of the mineral is thus NiSb. B. H. B.

Chemical Composition of Butyrellite. By W. I. Macadam (*Min. Mag.*, **6**, 175—180; *Zeit. Kryst. Min.*, **12**, 182).—In the investigation of ten samples of bog-butter or butyrellite (Dana) from various localities in the peat bogs of Scotland and Ireland, the author found that the portion of the butyrellite soluble in ether corresponded in all respects with the substance obtained under like conditions from ordinary butter. This portion varies in the ten analyses from 91·52 to 98·94 per cent. The portion insoluble in ether, 0·38 to 4·56 per cent., was slightly soluble in water, and gave evidence of the presence of milk-sugar. The portion insoluble in water contained nitrogen, and gave on combustion the peculiar odour of burning cheese. The ash or mineral portion, 0·01 to 0·36 per cent., contained traces of phosphoric acid. These results, and the fact that a number of cow's hairs were found in the samples, show that butyrellite has no claim to be called a mineral. It cannot be discussed how these masses found their way into the positions from which they are now obtained. It is, however, obvious that the material is not of mineral or even of resinous origin, but of undoubted animal derivation, and should therefore be erased from the list of minerals. B. H. B.

Minerals from Vesuvius. By E. Scacchi (*Zeit. Kryst. Min.*, **12**, 202—203).—1. *Hydrogiobertite* is the name given by the author to a new hydrated magnesium carbonate, which occurs in the form of grey, compact masses 2 to 15 mm. in diameter. With the lens, minute magnetite crystals are observed enclosed in the mass. The sp. gr. is 2·149 to 2·174. The loss on ignition amounted to 53·07 per cent. Of the sample, 0·507 gram contained 0·0025 gram of magnetite, and 0·022 gram of ferric oxide which was subtracted as limonite with the magnetite. The results of the analysis were as follows:—

CO_2.	MgO.	H_2O.	Total.
25·16	44·91	29·93	100·00

The formula of the new mineral is $Mg_2CO_4 + 3H_2O$.

The hydrogiobertite was discovered near Pollena in a block of augitophyre very closely resembling lava. In the interior, the structure was crystalline. On this rock was a compact mixture of silicates (plagioclase, augite, and magnetite) with which the hydrogiobertite was associated.

2. *Altered Aragonite.*—In the mother-rock of the hydrogiobertite, described above, hexagonal prisms, 3—4 mm. long and 1—1·5 mm. broad were found. They are white and opaque, and for the most part soluble in acids; the insoluble portion frequently preserving the original form of the crystal, or becoming divided longitudinally into prismatic fragments. On heating at 170°, there was a loss of 6·81 per cent. In hydrochloric acid, 11·78 per cent. was insoluble; this portion was found to contain 58·97 per cent. of silica with ferric oxide, alumina, and lime; whilst the soluble portion consisted essentially of lime. The insoluble substance also occurs in the interior of the crystals.

3. *Fluorspar.*—A number of minute octahedral crystals occurring on a lava from Pollena (1872) were found to be fluorspar. This mineral has hitherto been unknown in the lavas of Vesuvius and other volcanoes. Associated with the fluorspar are minute acicular crystals of apatite. B. H. B.

Chemical Constitution of Barytocalcite and Alstonite. By A. Becker (*Zeit. Kryst. Min.*, **12**, 222—227).—The monoclinic barytocalcite and the rhombic alstonite have hitherto been regarded as having the same chemical composition ($BaCO_3 + CaCO_3$). The question now arises whether they should both be considered isomorphous mixtures of $BaCO_3$ and $CaCO_3$, or whether one of them is not a molecular compound of the two carbonates with the formula $BaCaC_2O_6$. Groth regards barytocalcite as a molecular compound of this kind, whilst alstonite, he thinks, is an isomorphous mixture of equal amounts of the two salts. This view is confirmed experimentally by the author, who gives the following results of a series of analyses of the two minerals in question:—

	BaO.	CaO.	MnO.	CO_2.	Insol. res.	Total.
I.	50·09	19·77	0·35	29·52	—	99·73
II.	50·36	19·22	0·25	29·44	0·30	99·57
III.	51·59	18·61	0·35	29·39	0·28	100·22
IV.	44·69	23·40	0·29	31·71	—	100·09
V.	37·41	29·06	0·30	32·21	—	98·98
VI.	50·97	19·83	—	29·65	0·25	100·70
VII.	51·45	19·89	0·20	29·52	—	101·06

All the specimens analysed were from Alston Moor.

I. Barytocalcite, purchased from Stürtz of Bonn. II. Barytocalcite, purchased from Pech of Berlin. III. Barytocalcite from the

mineralogical museum of the University of Leipzig. These three analyses correspond with the formula $BaCO_3 + CaCO_3$.

IV. Alstonite from Pech of Berlin; formula $3BaCO_3 + 4CaCO_3$. V. A second specimen of the same, formula $BaCO_3 + 2CaCO_3$. VI. Alstonite, purchased from Gregory of London, formula $BaCO_3 + CaCO_3$. VII. Alstonite from the mineralogical museum of the University of Leipzig, formula $BaCO_3 + CaCO_3$.

For the three specimens of barytocalcite analysed, the same formula ($BaCO_3 + CaCO_3$) is obtained; so that this mineral must be regarded as a molecular compound; whilst of the four specimens of alstonite analysed, two had the same formula ($BaCO_3 + CaCO_3$), and the other two the formulæ $3BaCO_3 + 4CaCO_3$ and $BaCO_3 + 2CaCO_3$. Alstonite, consequently, is undoubtedly an isomorphous mixture of the two carbonates. B. H. B.

Chemical Composition of Herderite. By A. Des Cloizeaux and A. Damour (*Zeit. Kryst. Min.*, **12**, 204).—Since Des Cloizeaux (Abstr., 1884, 827) established the optical identity of the herderite crystals from Stoneham, Maine, and from Ehrenfriedersdorf, Saxony, C. Winkler (Abstr., 1884, 1102) has given an analysis of the crystals from both localities, attributing the loss to water, and not to fluorine. Subsequently F. A. Genth (Abstr., 1885, 488) found 8·93 per cent. of fluorine in the Stoneham herderite. These discordant results have induced the authors to make a fresh investigation, and their analysis shows the presence of a considerable amount of fluorine. The sp. gr. of the mineral examined was 2·98 (compare Abstr., 1885, 359).

B. H. B.

Minerals from Tuscany. By L. Busatti (*Zeit. Kryst. Min.*, **12**, 200—202).—At Caprillone, near Montecatini, fine, large crystals of barytes are found in geodes in conglomerate and miocene marl-limestone. The crystals are opaque, porcelain-white at the edges, and reddish-yellow in the middle. In appearance, the crystals resemble those of celestine. Analysis gave the following results:—

Ba.	Ca.	SO_4.	Total.	Sp. gr.
57·82	0·24	41·09	99·15	4·38

The author also describes a twin-crystal of hæmatite from Rio in Elba, in the Pisa Museum, exhibiting the planes R, $\frac{1}{2}$R, $-\frac{1}{8}$R, $\frac{2}{5}$R3, $\frac{4}{3}$P2. The twinning axis is perpendicular to ∞R. Descriptions are also given of crystals of chlorite from Bottino in the Apuan Alps; quartz from the Cala dell' Allume ore-bed in the island of Giglio; gypsum from the same locality; pyrolusite from the manganese ore-bed of the Campese in the island of Giglio; and magnetite and epidote from Romito. B. H. B.

Rare Copper Minerals from Utah. By G. S. Mackenzie (*Min. Mag.*, **6**, 181—182; *Zeit. Kryst. Min.*, **12**, 182—183).—The author gives analyses of two minerals from the American Eagle Mine, Utah Territory, occurring in intimate association with olivenite and other copper compounds. The results of the analyses were as follows:—

	CuO.	CaO.	MgO.	ZnO.	Ag.	Fe_2O_3.	Al_2O_3.	As_2O_5.
I.	28·59	19·67	0·61	2·75	0·29	0·45	—	39·80
II.	26·88	0·55	0·23	—	—	26·94	1·17	34·62

	P_2O_5.	H_2O.	CO_2.	Quartz.	Total.
I.	0·20	5·55	(0·98)	1·11	100·00
II.	—	9·25	—	0·71	100·35

I. *Conichalcite* in emerald-green globules. II. *Chenevixite* scattered in patches throughout such parts of the ore as occur in hard lumps, in a greenish opaque body with no lustre (compare Abstr., 1886, 516). B. H. B.

Columbite. By E. S. Dana (*Zeit. Kryst. Min.*, **12**, 266—274).—In 1861 Schrauf published his monograph on this mineral, in which the axial ratio is stated to be $a : b : c = 0{\cdot}40744 : 1 : 0{\cdot}33467$. The author has now made an exhaustive investigation of the recently discovered crystals from Standish in Maine. He gives a list of the 13 planes observed, and finds the axial ratio to be $a : b : c = 0{\cdot}40234 : 1 : 0{\cdot}35798$. The angles calculated from this ratio, on the whole, agree better with those given by Dana (1837) and Des Cloizeaux (1851) than with those given by Schrauf. The frequently repeated question whether columbite does not belong to the monosymmetric system like wolfram, is answered by the author in the negative. There can be no doubt that columbite crystallises in the rhombic system. B. H. B.

Plagioclase from California. By K. von Chroustschoff (*Zeit. Kryst. Min.*, **12**, 204—205).—The felspar examined forms large dark tabular crystals in a hypersthenite from San-Diego. The angles made by the directions of extinction with the edge formed by the faces 0P and $\infty\breve{P}\infty$, on cleavage plates taken parallel to 0P is $+1°$ to $+2°$, on plates parallel to $\infty\breve{P}\infty$ $+12°$. Analysis gave the following results :—

SiO_2.	Al_2O_3.	CaO.	Fe_2O_3.	MgO.	K_2O.	Na_2O.
65·17	21·04	1·20	0·74	0·04	1·70	9·20

Loss on ignition.	Total.	Sp. gr.	
0·80	99·89	2·659	B. H. B.

Oligoclase. By A. Des Cloizeaux and F. Pisani (*Zeit. Kryst. Min.*, **12**, 204).—A flesh-coloured felspar from Telemarken (Norway) with a cleavage angle $\infty\breve{P}\infty$: 0P, equal to 86° 30′, proves to be an oligoclase of the first class (Abstr., 1886, 776). The extinction on plates parallel to 0P is $+1°$ to $2\frac{1}{2}°$, parallel to $\infty\breve{P}\infty$ $+10°$ to 12°. Analysis gave the following results (I) :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Loss on ignition.	Total.	Sp. gr.
I.	65·30	23·00	—	2·42	9·65	0·70	0·20	101·27	2·610
II.	62·25	24·80	0·25	4·90	7·80	0·80	0·20	101·00	2·628

For comparison, an analysis (II) of sunstone from Frederiksvärn (*Zeit. Kryst. Min.*, **11**, 648) was made. As in the sunstone from Tvedestrand, the percentage of ferric oxide is very small in spite of the large amount of hæmatite particles intermingled. B. H. B.

Botryogene. By J. Hockauf (*Zeit. Kryst. Min.*, **12**, 240—254).—The author gives the results of two analyses of botryogene from the Vienna Museum. The specimen examined formerly belonged to Haidinger, and probably supplied the material for his original investigations. The analytical results were as follows:—

	SO_3.	Fe_2O_3.	MnO.	FeO.	CaO.	MgO.	H_2O.	Residue.	Total.
I.	37·12	18·31		2·24	0·75	7·91	34·10	0·34	100·77
II.	37·00	16·69	1·93	2·24	1·06	7·40	34·10	0·30	100·72

The formula adopted by the author is $5R''SO_4 + 2(Fe_2S_2O_9) + 38H_2O$. A mineral is frequently sold by the dealers as botryogene, which is not identical with it. There is a specimen thus obtained in the Vienna Museum, an analysis of which gave the following results:—

SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
33·53	4·52	1·93	2·09	2·34	0·79	5·44	48·68	99·32

(Compare Blaas, Abstr., 1884, 269, 1103.) B. H. B.

Flexibility of Itacolumite. By G. Spezia (*Zeit. Kryst. Min.*, **12**, 202).—The author was induced to test the accuracy of the general theory as to the cause of the flexibility of itacolumite by the fact that the flexible mica-like mineral occurs but sparsely in the itacolumite of North Carolina. His observations show that the rock is flexible when it is composed exclusively of quartz-grains. Under the microscope each separate grain is seen to be distinctly flexible. This may also be observed in the coarsely granular itacolumite from Mariaña in Brazil. The itacolumite examined is also very porous, as is shown by the rapid absorption of liquids. A prism weighing 186·444 grams absorbed 5·825 grams of distilled water, and had a volume of 73·5 c.c., of which 5·825 c.c. were of course taken up by the absorbed water, and thus represent the intergranular space. The tenacity of this itacolumite is also remarkable. The fracture of a prism 6·29 square cm. in section, by tension in the direction of the plane of cleavage and longitudinal axis of the flexible mica-like lamellæ, was effected with a load of 29·66 kilos. (= 67·06 lbs. per square inch). This tenacity is obviously due to the twisting of the quartz-grains, whilst the porosity is due to their power of moving. Consequently, the flexibility of itacolumite may be explained mechanically from the form and relative position of the quartz-grains, without assuming a flexible mineral. This conclusion is in accordance with the author's observations that rectangular prisms cut in different directions exhibit uniform flexibility. B. H. B.

Volcanic Fragments from the Lake of Bracciano. By G. Strüver (*Zeit. Kryst. Min.*, **12**, 197—200).—Numerous volcanic

fragments have recently been discovered in the district between l'Anguillara and the Lake of Martignano, in the midst of an enormous heap of angular fragments of limestones, leucitic and tephritic lavas, leucite phonolites, and trachytes. Similar materials have been found at Monte S. Angelo and near Cesano, in grey tuff. In these volcanic fragments, the following minerals have been found:—Pleonast, magnetite, limonite, wollastonite, pyroxene, hornblende, garnet, idocrase, humboldtilite, meroxene, sarkolite, nepheline, hauyn, leucite, anorthite, sanidine, titanite, apatite, and calcite. Of these minerals, *sarkolite* is the most interesting, as it has hitherto only been observed as a rare mineral in the Somma volcanic bombs. The crystals are 10 mm. long, 10 mm. broad, and 5 mm. deep. The combinations observed are 0P. ∞P∞. P, and 0P. ∞P∞. P. P∞. $\frac{1}{3}$P. ∞P. 3P3. Fracture conchoidal, vitreous lustre, flesh colour or colourless, translucent to transparent, streak white, hardness 6, optically uniaxial, double refraction positive. B. H. B.

Cosmical Powder which fell on the Cordilleras, near San Fernando, Chili. By A. E. Nordenskiöld (*Compt. rend.*, **103**, 682—686).—This powder fell for about half an hour on the surface of fresh fallen snow on the Cordilleras, in November, 1883. During this month a peculiar red glow was observed in the sky in the evening, and the atmosphere was highly charged with electricity. The powder was collected by C. Stolp and forwarded to the author. It consists mainly of irregularly rounded reddish-brown grains, frequently agglomerated in somewhat large masses, which showed no signs of fusion, and dissolved, though slowly, in hydrochloric acid. The powder also contained a small quantity of annular scales, probably felspar and green hexagonal plates, which consisted chiefly of mica. No metallic iron was present. The powder had the following composition:—Fe_2O_3, 74·59; NiO, with traces of CoO, 6·01; CuO, traces; P_2O_5, 0·63: SO_3, 0·37; SiO_2, 7·57: Al_2O_3, 2·90; CaO, 0·31; MgO, 3·88; loss on heating, 2·61 = 98·87. A small quantity of alkali is probably also present.

The composition of the powder shows that it is not a product of the Krakatoa eruption, and is not of terrestrial origin. It is evidently of cosmical origin, but there is no proof that the red glow in the sky was in any way connected with the fall of the powder.

C. H. B.

Meteorite in a Tertiary Lignite. By Gurlt, with Note by Daubrée (*Compt. rend.*, **103**, 702—703).—The meteorite was found in a block of tertiary lignite from Wolfsegg. It formed a rectangular parallelopiped 67 mm. by 62 mm. by 47 mm., and weighed 785 grams. The surface showed cupules similar to those observed on meteorites, and was covered with a thin layer of magnetic oxide of iron. The meteorite is a holosiderite, and contains carbon with a trace of nickel, but no quantitative analysis was made. It showed cubical cleavage, but a polished surface did not show Widmanstatt's figures when treated with acid.

Daubrée considers that the position of the meteorite and other

evidence proves that the "meteorite" was deposited in the lignite during the formation of the latter. C. H. B.

Note by Abstractor.—Lawrence Smith has shown (Abstr., 1879, 892) that the native iron found in the miocene lignites of Greenland is really of terrestrial origin. C. H. B.

Analysis of Mineral Springs in Aegina and Andros. By A. K. Dambergis (*Ber.*, **19**, 2538—2540).—The water from Aegina springs from a calcareous rock, has a salt taste, and a temperature of 26°; sp. gr. at 12° = 1·009635; 10,000 c.c. of the water contain—

Calcium sulphate	12·3757	grams.
Sodium carbonate	4·2400	„
„ chloride	84·0915	„
Potassium chloride	1·9455	„
Magnesium bromide	0·3050	„
„ chloride	15·4679	„
Calcium carbonate	0·8501	„
Magnesium carbonate	3·4391	„
Iron carbonate	0·0160	„
Alumina	0·0200	„
Silica	0·1600	„
Carbonic anhydride (half combined)	4·1004	„
Free carbonic anhydride	1·4150	„

Traces of strontia, fluorine, iodine, nitric and phosphoric acids, ammonia, lithia, and organic substances are also present in the water.

The water of Andros has an agreeable taste, is colourless and without odour; it is used on account of its medicinal properties; 10,000 c.c. of the water contain—

Sodium carbonate	0·12046	gram.
Calcium „	0·83000	„
Magnesium carbonate	0·25140	„
Calcium sulphate	0·24010	„
Sodium chloride	1·11996	„
Potassium chloride	0·09586	„
Magnesium „	0·18192	„
Alumina	0·06000	„
Silica	0·14400	„
Carbonic anhydride (half combined)	0·54680	„
„ „ (free)	0·15640	„

Traces of iron carbonate, ammonia, nitric and phosphoric acids, and organic substances were also found to be present. N. H. M.

Organic Chemistry.

Volatility of Methane-derivatives. By L. Henry (*Compt. rend.*, **103**, 603—606).—The volatility of methane-derivatives follows the same order as that of the substituted elements when the latter are arranged in natural families in the order of their atomic weights. The boiling point rises as the molecular weight increases, but the differences between the volatility of the methane-derivatives are much less than those between the boiling points of the electronegative elements which they contain.

	B. p.	Diff.		B. p.	Diff.
Cl, gas	— 33°	96°	MeCl, gas	— 23°	27·5
Br, liquid	+ 63		MeBr, gas	+ 4·5	
I, solid	+ 250	187	MeI, liquid ...	44	39·5
O, gas.....	— 181	629	Me_2O, gas	— 23	60·0
S, solid	+ 448		Me_2S, liquid ...	+ 37	
N, gas	— 193	480	Me_3N, gas	+ 9	50·0
P, solid	+ 287		Me_3P, liquid ...	+ 41	

The differences show that electronegative elements in the same natural family are far from being comparable in the free state, whilst in methane-derivatives they may be regarded as existing under analogous physical conditions.

In each of the groups of methane-derivatives, the rise of the boiling point is not proportional to the increase in the molecular weight; in fact the greater the increase in the molecular weight resulting from substitution, the less proportionally is the rise of the boiling point. The substitution of sulphur causes proportionally less rise in the boiling point than the substitution of oxygen, and the substitution of phosphorus less than the substitution of nitrogen, although sulphur and phosphorus are solids, whilst oxygen and nitrogen are gases.

The atomic weights being nearly equal, the diminution of volatility resulting from substitution is greater the more strongly marked the electronegative character of the substituted element, or, in other words, the more distinctly its properties differ from those of hydrogen. This is well seen in the case of the nitrogen- and boron-derivatives.

Me_3N, mol. wt. 59, a liquid boiling at 9·3°.

Me_3B, mol. wt. 56, a gas which liquefies at —10° under a pressure of 3 atmos.

This phenomenon is doubtless connected with the fact that the heat of combination of carbon with electronegative elements diminishes as the atomic weight of the latter increases. C. H. B.

Sugars. By Berthelot (*Compt. rend.*, **103**, 533—537).—A solution of invert sugar which had been kept for nearly 30 years, deposited spheroidal groups of radiating crystals, which when care-

fully dried on filter-paper resembled purified glucose. The crystals have the composition $C_6H_{12}O_6$ when anhydrous; their reducing power is equal to that of glucose, and they are completely fermentable, but their rotatory power is only $[\alpha]_D = +32{\cdot}2$, or little more than half that of glucose. The crystals are a compound of glucose and levulose, in which one constituent behaves like water of crystallisation. The compound is decomposed by solvents; its rotatory power shows that the ratio of levulose to glucose is 1 : 5. A similar compound prepared by Gélis has the rotatory power of +15°, which corresponds with a ratio of levulose to glucose of 1 : 3.

The compound formed as an intermediate product in alcoholic fermentation is most probably formed by the union of one molecule of levulose with two of glucose, but it does not seem to have been obtained in crystals.

In the process of extracting raffinose from cotton-seed cake, crystals were obtained which when dried on filter-paper without treatment with any solvent had all the properties of mellitose from the manna of eucalyptus. When the aqueous solution of this substance is treated with yeast, only half the sugar undergoes fermentation, and the liquid contains a non-fermentable sugar with the properties of eucalyne. If the mellitose is treated with boiling alcohol, it splits up into raffinose, which crystallises after some time, and eucalyne, which remains in solution. An alcoholic solution of raffinose and eucalyne when allowed to remain, deposits crystals which seem to be formed by the recombination of the raffinose with the eucalyne.

Mellitose, which is widely diffused in the vegetable kingdom, is the result of the association of raffinose, a true saccharose, with eucalyne, a non-fermentable carbohydrate. This association bears no resemblance to the union of glucoses to form saccharoses, and the constitution of mellitose is analogous to that of hydrates and alcoholates rather than to that of ethereal salts. C. H. B.

Sugar formed in the Inversion of Lichens. By P. Klason (*Ber.*, **19**, 2541).—Bauer showed (Abstr., 1886, 869) that dextrose is formed by inverting lichens. The author previously obtained the same results (*Lund's Fysiogr. Sällskops Minneskr.*, 1878, 61). Apparently no other sugar is formed in the inversion. N. H. M.

Action of Dilute Acids on Grape-sugar and Fruit-sugar. By M. Conrad and M. Guthzeit (*Ber.*, **19**, 2569—2574).—According to Tollens and v. Grote (*Annalen*, **175**, 181, and **206**, 207), dextrose as well as levulose when boiled with sulphuric, or better with hydrochloric acid, yields acetopropionic acid in very small quantity.

Quantitative experiments on the decomposition of cane-sugar by hydrochloric acid, made by the authors (Abstr., 1885, 745), pointed to the formation of a small amount of acetopropionic acid from dextrose. Experiments described in the present paper show that this view (the formation of acetopropionic acid chiefly from levulose) only holds good for the decomposition of cane-sugar with dilute sulphuric acid, and not with hydrochloric acid.

Quantities of dextrose and levulose corresponding with 20 grams of

cane-sugar were heated for 17 hours with the same amounts of acid and water as those previously used (*loc. cit.*).

1. Decomposition with dilute sulphuric acid—

		Humic substances.	Dextrose.	Aceto-propionic acid.	Formic acid.
Dextrose.....	52·6	0·83	43·70	2·78	1·21
Levulose.....	52·6	13·78	—	16·78	6·46
Cane-sugar....	100·0 =	14·61	43·70	19·56	7·67

2. Decomposition with dilute hydrochloric acid—

		Humic substances.	Dextrose.	Aceto-propionic acid.	Formic acid.
Dextrose.....	52·6	4·76	14·52	15·53	6·51
Levulose.....	52·6	10·65	—	16·28	8·78
Cane-sugar....	100·0 =	15·41	14·52	31·81	15·29

N. H. M.

Decomposition of Milk-sugar by Dilute Hydrochloric Acid. By M. Conrad and M. Guthzeit (*Ber.*, **19**, 2575—2576).—The following results were obtained from three experiments, in which 21, 21, and 10·5 grams of milk-sugar were heated with 50 c.c. of water and 4·87, 5·0, and 4·87 grams of hydrochloric acid respectively :—

	Humic substances.	Milk-sugar (unchanged).	Acetopropionic acid.	Formic acid.
1	3·68	5·54	6·29	2·39
2	3·94	—	5·80	2·24
3	1·60	—	3·32	1·33

In 2 and 3, the milk-sugar was not determined. N. H. M.

Carbohydrates. By O. Wallach (*Annalen*, **234**, 364—375).—The rhizome of the water lily, *Iris pseudacorus*, contains a peculiar carbohydrate, called "irisin" by the author. *Irisin*, $C_6H_{10}O_5 + H_2O$, closely resembles inulin, but is distinguished from the latter by its more powerful action on polarised light; $[\alpha]_D = -49°\ 90$ for a 2 per cent. solution of irisin, and $[\alpha]_D = -37°\ 27'$ for a solution of inulin of the same strength. Fehling's solution is not reduced by irisin, but the carbohydrate is easily attacked by dilute acids, yielding levulose as the chief product. Irisin is four times as soluble as inulin in water at 22°. Under the microscope, the globules of irisin resemble the minute globules of inulin in size, but they do not exhibit double refraction. W. C. W.

Animal Gum. By H. A. Landwehr (*Pflüger's Archiv*, **39**, 193—204).—The animal carbohydrates may be arranged in parallel groups with those occurring in the vegetable kingdom, and animal gum resembles vegetable gum in yielding oxalic acid after treatment with nitric acid. It is obtained readily from mucin. Mucin was prepared

by precipitation with acetic acid from an extract of submaxillary glands, made with a 1 per cent. sodium carbonate solution. The precipitate was washed with weak acetic acid, and then dissolved in weak hydrochloric acid by the aid of heat. On neutralising with soda, a white flocculent precipitate is obtained, which is increased in amount on the addition of sodium sulphate and boiling. The precipitate is collected and freed from salt by dialysis; it consists of an ordinary proteïd. The filtrate contains no nitrogen, but contains animal gum. From tendon mucin, the same carbohydrate is obtained, in spite of what Loebisch (Abstr., 1886, 166) says to the contrary; it may also be obtained from synovia, colloïd cysts, and from the mucin of the snail's mantle. Mucin and animal gum both yield lævulic acid when treated with hydrochloric acid.

Another source of animal gum is chondrin. By long boiling with water, chondrin splits into gelatin, animal gum, and possibly a third substance not yet further investigated. Pure chondrin is soluble in hot water, and its solutions gelatinise when cold, if not too dilute; this power of gelatinising is lost after prolonged boiling. A dilute solution gives the following reactions:—Dilute mineral acids cause a precipitate soluble in excess; acetic acid gives a precipitate insoluble in excess; acetic acid and potassium ferrocyanide give a precipitate, soluble in excess of the latter reagent. Sodium chloride solution gives no cloud, but hinders the precipitation by acetic acid. Metaphosphoric acid gives a cloudiness disappearing on warmth. Alum gives a cloudiness, disappearing on adding excess. Lead acetate gives a precipitate, soluble in excess. Basic lead acetate gives a precipitate, partially soluble in excess. Lead acetate and ammonia give a flocculent precipitate, insoluble in excess. Tannin and acetic acid give a precipitate, insoluble in excess. Copper sulphate and sodium hydroxide colour the liquid violet, which becomes red on boiling. Boiling the solution for five or six hours with 1 per cent. sulphuric acid gives it the power of reducing copper salts, this being due to the formation of a reducing sugar from animal gum. Animal gum may be separated from chondrin in the same way as from mucin.

Metalbumin and paralbumin may also be used as sources of animal gum. It is also found in small quantities, but constantly in the red blood corpuscles, brain, kidney, spleen, liver, and pancreas. Proteïds proper do not yield it. W. D. H.

Derivatives of Thioformaldehyde. By A. Wohl (*Ber.*, **19**, 2344—2347).—*Thiometaformaldehyde*, $(CH_2S)_2$, is obtained when an aqueous or alcoholic solution of hexamethyleneamine saturated with hydrogen sulphide is heated on a water-bath. It separates as a white, amorphous substance, which is washed with water and hydrochloric acid, and extracted with boiling glacial acetic acid and alcohol. It is insoluble in all the usual solvents, and has a peculiar odour; it melts at 175—176°, and decomposes at a high temperature. It dissolves unchanged in strong sulphuric acid.

Methylthioformaldine, $S_2(CH_2)_3NMe$, is prepared by diluting 50 c.c. of a 20 per cent. solution of formaldehyde with an equal volume of water, and saturating with hydrogen sulphide; 200 c.c. of water are

then added, the whole filtered and stirred with 20 c.c. of a 30 per cent. solution of methylamine. In 24 hours crystals separate. More hydrogen sulphide is then passed through the solution until it is no longer turbid; the crystals are collected, washed with water, and dissolved in ether. It crystallises in needles melting at 65°, and is insoluble in water, soluble in dilute mineral acids, alcohol and glacial acetic acid. It distils with steam, boils at about 185°, being at the same time converted into a compound melting at 130—140°. The *hydrochloride* forms needles readily soluble in water; it melts at 188° with decomposition.

Dimethylthioformaldinium iodide, $S_2(CH_2)_3NMe_2I$, is formed by treating the compound with methyl iodide. In two to three days the liquid solidifies to a mass of slender, lustrous needles. It melts at 161—163°, and dissolves readily in water, sparingly in alcohol. The *platinochloride*, $[S_2(CH_2)_3NMe]_2Me_2PtCl_6$, is a bright yellow, crystalline substance. The iodide dissolves in hot aqueous potash and separates unchanged on cooling. When boiled with silver oxide, it yields an ammonium base, which, however, could not be isolated.

N. H. M.

Chloro-derivatives of Acetals. By O. Magnamini (*Gazzetta*, **16**, 330—333).—*Trichloromethylethylacetal*, $CCl_3{\cdot}CH(OMe){\cdot}OEt$, is obtained by heating tetrachlorether with methyl alcohol in sealed tubes. The reaction is as follows: $CCl_3{\cdot}CHCl{\cdot}OEt + MeOH = HCl + CCl_3{\cdot}CH(OMe){\cdot}OEt$. It is a colourless liquid of camphor-like odour; it boils at 193·4; sp. gr. = 1·32.

Trichlorodimethylacetal, $CCl_3{\cdot}CH(CMe)_2$, obtained from tetrachlorethyl methyl ether, is a liquid of similar characters. It boils at 183·2°; sp. gr. = 1·28.

The *tetrachlorethyl methyl ether*, $CCl_3{\cdot}CHCl{\cdot}OMe$, prepared by the action of phosphoric chloride on chloral methylate, is a colourless liquid boiling at 178°; sp. gr. at 0° = 1·84. It does not appear to have been previously isolated.

V. H. V.

Diisonitrosoacetone. By H. v. Pechmann and K. Wehsarg (*Ber.*, **19**, 2465—2467).—V. Meyer and Züblin have shown that when acetoacetic acid is treated with nitrous acid, carbonic anhydride is evolved, and isonitrosoacetone formed. The authors find that when, in like manner, acetonedicarboxylic acid is treated with water and sodium nitrite, a rapid evolution of carbonic anhydride takes place, and *diisonitrosoacetone*, $CO(CH{\cdot}NOH)_2$, is produced. This forms glistening prismatic crystals, melting with decomposition at 143—144°. It is easily soluble in alcohol and ether, sparingly in cold water, chloroform, and benzene. It is very unstable, and detonates when heated. Its aqueous solution when heated decomposes into hydrocyanic acid, carbonic anhydride, and water. Acids cause a similar decomposition, but hydroxylamine is also among the products. It is more stable in alkaline solutions, and forms *alkali salts*, which crystallise in orange-yellow needles. Its salts, especially the red crystalline *silver* salt, explode when heated. When warmed with phenol and sulphuric acid, the nitroso-compound gives a red coloration, with ferric chloride a brown. The authors are further investigating the subject.

L. T. T.

Ketines. By L. Œconomides (*Ber.*, **19**, 2524—2527).—When a very dilute solution of diethylketine, $C_{10}H_{16}N_2$, is treated with the theoretical amount of potassium permanganate, a ketinedicarboxylic acid is obtained, identical with that prepared by Wleügel by reducing ethyl isonitrosoethylacetate (Abstr., 1882, 949). If the oxidation takes place in a warm solution, other and more unstable acids are formed. When 5 grams of ethyl imidoisonitrosobutyrate are carefully warmed with powdered zinc chloride at 60—70° for a long time, and the product saponified with alcoholic potash, a small quantity of an acid melting at 190—195°, identical with Wleügel's acid (*loc. cit.*), is formed. The above reactions, together with the fact that the ketine-acid does not yield an anhydride, point to the following constitutional formulæ for methylketine and the ketine-dicarboxylic acid:—

$$N\lessdot\begin{matrix}CMe\cdot CH\\CH:CMe\end{matrix}\gtrdot N \text{ and } N\lessdot\begin{matrix}CMe\cdot C(COOH)\\C(COOH):CMe\end{matrix}\gtrdot N.$$

N. H. M.

Pure Butyric Acid. By A. Bannow (*Ber.*, **19**, 2552—2554).—Pure butyric acid is best prepared by converting the commercial acid into the ethyl salt, which is then fractionally distilled. The fraction boiling at 120—121° is reconverted into acid. N. H. M.

Derivatives of Tiglic Acid. By P. Melikoff (*J. Russ. Chem. Soc.*, 1886, 287—297).—Tiglic (methylcrotonic) acid,

$$CHMe:CMe\cdot COOH,$$

was prepared either by the saponification of the oil of Roman chamomile (Kopp, Abstr., 1879, 454), or by heating α-methyl-β-hydroxybutyric acid (Rohrbeck, Abstr., 1878, 136). The acid was treated under water with an aqueous solution of hypochlorous acid, the product of the reaction extracted with ether, and the solvent distilled off. The residue, after remaining for some time over sulphuric acid, solidified to a crystalline mass, which was found to consist of two isomeric chlorhydroxyvaleric acids, $C_5H_9ClO_3$. A concentrated aqueous solution of this mixture was neutralised with zinc carbonate: a crystalline zinc salt was precipitated, and the mother-liquor on being evaporated left another salt in the form of an amorphous humoïd substance. The two acids obtained by decomposing these salts with sulphuric acid are both easily soluble in water, alcohol and ether; the one forming a crystalline sparingly soluble zinc salt, melts at 75°, and crystallises from ether in thin prisms; the other isomeride melts at 111·5°, and is obtained from its ethereal solution in the form of large, translucent prisms.

When a mixture of these acids, or each of them separately, is treated with alcoholic potash, the potassium salt of an anhydro-acid, $\lessdot\begin{matrix}CHMe\\—O—\end{matrix}\gtrdot CMe\cdot COOH$, is formed. The free acid forms silky, crystalline needles having the odour of butyric acid, easily soluble in water, alcohol, and ether, melting at 62°. The energy with which it enters into direct combination is in the main the same as that shown by β-methylglycidic acid: α-methylglycidic acid in this respect exhibiting

much greater energy. This circumstance, established by experiments on the hydration of the potassium salt by heating with water, is in accordance with the results obtained by the author in a former work on glycidic and α- and β-methylglycidic acids (Abstr., 1885, 650). The energy of direct combination is diminished with increasing molecular weight in acids of analogous constitution; at the same time among isomeric acids the greatest energy is exhibited by the one containing tertiarily united carbon in its molecule. α-β-Dimethylglycidic acid contains one CH_2-group more than α- and β-methylglycidic acids, but, on the other hand, one of its carbon-atoms combined with oxygen is in tertiary union.

By the action of hydrochloric acid on α-β-dimethylglycidic acid, *α-methyl-β-chlor-α-hydroxybutyric acid*, OH·CHMe·CMeCl·COOH, is formed; it melts at 75°, and is identical with one of the chlorhydroxyvaleric acids above described, the other isomeride being therefore *α-methyl-α-chloro-β-hydroxybutyric acid*, CHMeCl·CMe(OH)·COOH. An aqueous solution of α-β-dimethylglycidic acid, when heated during 8—10 hours at 99°, is converted into *α-β-dimethylglycidic acid*, OH·CHMe·CMe(OH)·COOH, melting at 107°, readily dissolving in water, alcohol, and ether. A. T.

Constitution of Chlorhydroxybutyric and Dichlorobutyric Acid. By P. Melikoff (*J. Russ. Chem. Soc.*, 1886, 227—303).—Chlorhydroxybutyric acid (formed by the combination of crotonic with hypochlorous acid, Abstr., 1884, 1301, and 1885, 650), when heated with concentrated sulphuric acid, yields monochlorocrotonic acid, crystallising in long, thin prisms, melting at 98°, sparingly soluble in cold, more readily in hot water, easily soluble in alcohol and ether. This acid yields normal crotonic acid (m. p. 72°) on reduction by zinc and sulphuric acid. The chlorocrotonic acid above mentioned is an α-chlorinated product, the isomeric β-derivative being obtained, amongst other methods, by the action of phosphorus pentachloride on ethyl acetoacetate; hence, the chlorhydroxybutyric acid in question must be *α-chloro-β-hydroxybutyric acid*.

This acid was heated with hydrochloric acid, and *α-β-dichlorobutyric acid* was obtained; it crystallises in long prisms and melts at 69°. An alcoholic solution of the latter compound, when treated with alcoholic potash, gives α-monochlorocrotonic acid. α-β-Dichlorobutyric acid is formed in like manner when α-monochlorocrotonic acid is heated with hydrochloric acid. A. T.

Hydroxystearic Acids of Different Origin. By A. C. and M. Saytzeff (*J. Russ. Chem. Soc.*, 1886, 328—348).—A hydroxystearic acid was prepared by one of the authors some time ago in his work on the oxidation of oleic acid (Abstr., 1886, 140). Another acid of this composition was discovered by Frémy (*Annalen*, **19**, 296; **20**, 50; **33**, 10), who obtained it by the action of concentrated sulphuric acid on oleic acid, and described it under the name of hydromargaritic acid. Although the main points of the reaction had been satisfactorily explained by Frémy's work, yet subsequent work on this question has mostly led to unsatisfactory results. Sabaneieff

(Abstr., 1886, 442) has at last succeeded in throwing some new light on the processes involved, but the authors do not in all cases obtain results in agreement with his.

Oleic acid was obtained by the saponification of oil of almonds, and purified in the ordinary way by conversion into its lead salt. The action of sulphuric acid was regulated in such a manner as to prevent the temperature rising above 35°. The mixture was then allowed to remain 20 hours at a temperature below 0°, and decomposed by water. In order to increase the yield of hydroxystearic acid, the fatty layer, separated by the action of water and solidifying at the ordinary temperature to a crystalline mass, was treated with alcoholic potash, whereby the anhydrides of this acid are decomposed. The saponified product was then converted into the acid by boiling with sulphuric acid. When the products of the action of sulphuric acid on oleic acid are left for some time even at low temperatures, the quantity of hydroxystearic acid is diminished, whilst the quantity of its anhydrides increases. Hydroxystearic acid was extracted from the above-mentioned crystalline mass by repeated recrystallisation from ether and alcohol. So obtained, *hydroxystearic* acid,

$$CH_3\cdot(CH_2)_{13}\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot COOH,$$

melts at 83—85°, and resolidifies at 68—65°. At 20° alcohol (99½° Tr.) dissolves 8·78 per cent., ether 2·3 per cent. of the acid. Hydroxystearic acid does not absorb bromine. The free acid and the hydroxystearates of sodium, calcium, barium, copper, zinc, and silver, were analysed, and the formula of the acid shown to be $C_{18}H_{36}O_3$.

With hydriodic acid, hydroxystearic acid yields iodostearic acid, $CH_3\cdot(CH_2)_{13}\cdot CH_2\cdot CHI\cdot CH_2\cdot COOH$; the latter can be converted into ordinary stearic acid by reducing its alcoholic solution with zinc and hydrochloric acid.

When hydroxystearic acid is heated at 100° in sealed tubes with fuming hydrochloric acid, a syrupy liquid is formed, soluble in ether, insoluble in alcohol and water, and having the composition of oleic acid. It does not show acid properties, nor give additive products with bromine or iodine (in Hubl's solution); it is therefore considered to be a complete anhydride of hydroxystearic acid,

$$CO<\begin{matrix}O\cdot C_{17}H_{34}\\ C_{17}H_{34}\cdot O\end{matrix}>CO,$$

formed by elimination of 2 mols. of water from 2 mols. of the acid (analogous to glycolide or lactide). The anhydride is decomposed into hydroxystearic acid by treatment with alcoholic potash at temperatures above 150°. Heated with dilute sulphuric acid (in sealed tubes at 100°), hydroxystearic acid yields the same anhydride, but when concentrated sulphuric acid is used at ordinary temperature, two other products of non-saturated character are formed, one combining with 17 per cent., the other with 33 per cent., of iodine, when heated with it on the water-bath. These substances bear a great resemblance to Frémy's metoleic acid, and will be further investigated.

It was shown that the hydroxystearic acid prepared by the action

of moist silver oxide on iodostearic acid was identical with that described above.

Finally, the authors have studied the action of alcoholic potash on iodostearic acid. After heating the mixture in a reflux apparatus, and expelling the alcohol by distillation, the product of the reaction was decomposed by sulphuric acid. An acid was obtained, solidifying at ordinary temperatures to a crystalline mass, and consequently not identical with oleic acid. It was purified by converting it into the sodium salt, recrystallising this salt from alcohol, precipitating with zinc sulphate, recrystallising from boiling alcohol, and decomposing the zinc salt by sulphuric acid. Thus purified, the substance crystallises from ether in translucent, rhombic tables, easily soluble in alcohol, sparingly in ether, and melts at 40—45°. The composition of this acid was found to be the same as that of oleic and elaidic acids. It is a non-saturated compound, taking up two atoms of bromine or iodine. When oxidised by potassium permanganate in alkaline solution, it yields dihydroxystearic acid, melting at 78°. The authors intend to continue the investigation of this *solid oleic acid*. Another acid, melting at 20—25°, simultaneously formed by the action of potash on iodostearic acid, was found to be a mixture of ordinary and solid oleic acids. The constitution of solid oleic acid is $CH_3{\cdot}(CH_2)_{13}{\cdot}CH_2{\cdot}CH : CH{\cdot}COOH$, ordinary oleic acid being represented by $CH_3{\cdot}(CH_2)_{13}{\cdot}CH : CH{\cdot}CH_2{\cdot}COOH$. A. T.

Action of Trimethylene Bromide on Ethyl Acetoacetate, Benzoylacetate, and Acetonedicarboxylate. By W. H. Perkin, Jun. (*Ber.*, **19**, 2557—2561; comp. Abstr., 1886, 689).—When the acid $C_7H_{10}O_3$ (from trimethylene bromide and ethyl sodacetoacetate) is boiled with water, carbonic anhydride is evolved, and Lipp's acetobutyl alcohol (Abstr., 1886, 218) is formed. When the acid is distilled, the anhydride of acetobutyl alcohol, $CH_2<\begin{matrix}CH : CHMe\\ CH_2{\cdot}CH_2{-}\end{matrix}>O$, is obtained; it is a mobile oil. The same compound is also formed when acetobutyl is heated. Strong hydrobromic acid dissolves the ethyl salt $C_9H_{14}O_3$, and decomposes it into bromobutyl methyl ketone (Lipp, *loc. cit.*) and carbonic anhydride. Benzoyltetramethylenecarboxylic acid is decomposed by hydrobromic acid in a similar manner, with formation of the compound $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$; this crystallises in plates melting at 61°. The instability towards hydrobromic acid of the products obtained by the action of trimethylene bromide on ethyl acetoacetate and benzoylacetate respectively, distinguishes them sharply from tetramethylenedicarboxylic acid.

Trimethylene bromide acts on the sodium compound—

$$CO(CHNa{\cdot}COOEt)_2$$

(from ethyl acetonedicarboxylate and sodium ethoxide), yielding the compound $COOEt{\cdot}CH<\begin{matrix}C(CH_2{\cdot}COOEt)\\ CH_2{-}CH_2{-}CH_2\end{matrix}>O$. The latter is a colourless oil boiling at 238—240 (under 150 mm. pressure). The *monethyl salt* melts at 114°; the free acid at 185—190° with decom-

position. When the monethyl salt is distilled, a substance is obtained apparently identical with the product of the reaction between trimethylene bromide and ethyl acetoacetate. The dicarboxylic acid is decomposed by boiling water into acetobutyl alcohol and carbonic anhydride. N. H. M.

Ethyl Acetotrimethylenecarboxylate. By W. H. Perkin, Jun., and P. C. Freer (*Ber.*, **19**, 2561—2569).—The fact that trimethylene bromide reacts with ethyl malonate, yielding a tetramethylene-derivative, and with ethyl acetoacetate with formation of an ether, suggested the possibility that the product of the reaction between ethylene bromide and ethyl acetoacetate (Trans., 1885, 801) is not a trimethylene-derivative but an ether. The results of determinations of the magnetic circular polarisation, and the optical properties point, however, to the trimethylene formula first ascribed to the compound.

Ethylic bromethylacetoacetate, $CH_2Br{\cdot}CH_2{\cdot}CHAc{\cdot}COOEt$, is obtained by dissolving ethyl acetyltrimethylenecarboxylate, well cooled, in hydrobromic acid, sp. gr. 1·85 (3 parts); after being left for 10 minutes at the ordinary temperature, it is poured into ice water. It is a yellowish oil, having an odour of camphor; when exposed to air it becomes brown, and gives off hydrobromic acid. When reduced by means of zinc-dust and acetic acid, it is converted into ethyl acetoacetate.

Acetopropyl alcohol, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is prepared by boiling 20 grams of the above bromo-compound for two hours with 5 grams of hydrochloric acid and 20 grams of water. The reaction is analogous to that by means of which Lipp obtained acetobutyl alcohol from ethyl bromopropylacetoacetate (Abstr., 1886, 218). It is a colourless oil, very soluble in water; the solution very readily reduces ammoniacal silver solution but not Fehling's solution. It is very unstable. A phenylhydrazine-compound was prepared. When the alcohol is heated, it is converted with evolution of water into a mobile oil, having an ethereal odour; it is probably an *anhydride*,

$$CH\ll^{CMe\text{——}}_{CH_2{\cdot}CH_2}>O$$

(comp. Abstr., 1886, 219).

γ-Pentylene glycol, $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by reducing acetopropyl alcohol with sodium amalgam. It is a very thick, colourless oil, extremely soluble in water. It boils at 210—220° with partial decomposition. When heated above its boiling point, or with 50 to 60 per cent. of sulphuric acid at 100°, it is converted into the *anhydride*, $CH_2<^{CHMe\text{—}}_{CH_2{\cdot}CH_2}>O$, boiling at 78—83°.

Pentylene glycol dissolves in hydrobromic acid (sp. gr. 1·85) with considerable development of heat; when the solution is heated at 80°, the *monobromohydrin* of the glycol, $C_5H_{11}BrO$, is formed. This is a colourless oil, which boils (under 150 mm. pressure) at 144—145°.

N. H. M.

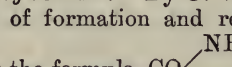
Derivatives of Diazosuccinic Acid. By T. Curtius and F. Koch (*Ber.*, **19**, 2460—2462).—This is a continuation of the authors' previous work on this subject (Abstr., 1885, 885). Aspartic acid was

obtained by the reduction of ethyl diazosuccinate with zinc-dust and acetic acid, thus proving the correctness of the formula formerly ascribed to diazosuccinic acid. *Methyl diazosuccinamate*,

$$NH_2{\cdot}CO{\cdot}CN_2{\cdot}CH_2{\cdot}COOMe$$

(from the action of ammonia on methyl diazosuccinate), crystallises in long, golden-yellow prisms soluble in ether and alcohol, and melting at 84°. When ethyl diazosuccinate is acted on by cold slightly acidified water, *malamic* and *fumaramic* acids are produced. Malamic acid, $NH_2{\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, crystallises in colourless prisms easily soluble in water, alcohol, and ether, and melts at 146°; its *methyl salt* yields silky scales soluble in alcohol, ether, and water, and melting at 105°. *Methyl fumaramate*, $NH_2{\cdot}CO{\cdot}C_2H_2{\cdot}COOMe$, crystallises in colourless plates, soluble in alcohol, and melts at 160—162°. *Ethyl benzoylmalamate*, $NH_2{\cdot}CO{\cdot}CH(OBz){\cdot}CH_2{\cdot}COOEt$, was obtained by heating together equal molecular proportions of benzoic acid and ethyl diazosuccinamate at 140—150°. It forms colourless clinorhombic crystals soluble in water, alcohol, and ether, and melts at 96—97°. It decomposes easily when heated. The corresponding *methyl salt* forms colourless crystals, melting at 78—80°. By the action of iodine on an ethereal solution of ethyl diazosuccinamate an unsymmetrical *ethyl diiodosuccinamate*, $NH_2{\cdot}CO{\cdot}CI_2{\cdot}CH_2{\cdot}COOEt$, is formed. This crystallises in long, greenish-white needles which darken at 110°, melt at 132°, and decompose at 150°. The *methyl salt* and corresponding *methyl* and *ethyl bromo-salts* are oils. L. T. T.

Dichloropyromucic Acid. By A. Denaro (*Gazzetta*, **16**, 333—335).—If a current of dry chlorine gas is passed into the ethyl salt of pyromucic acid, a thick oil is at first obtained, probably consisting of the tetrachloride of the acid. This on decomposition with alcoholic potash and subsequent acidification, yields a *dichloropyromucic acid* which crystallises in white needles, melting at 167°. Its *barium* salt crystallises with 3 mols. H_2O in prisms, the *calcium* salt with $3\frac{1}{2}$ mols. H_2O in scales; both become completely anhydrous when heated to 110°. V. H. V.

Constitution of Glycoluril. By O. Widmann (*Ber.*, **19**, 2477—2482).—As the mode of formation and reactions of this substance are best explained by the formula  , which undoubtedly belongs to acetylenecarbamide, the author has carefully re-examined these two compounds with the view of determining whether they are isomeric or identical. He finds that the latter is the case, and that the apparent differences in their reactions are due to erroneous observation. When boiled with concentrated baryta-water, acetylenecarbamide does not, as previously asserted, yield carbonic anhydride, but, like glycoluril, is decomposed into hydantoic acid and carbamide. The solubility of acetylenecarbamide is given by Schiff as 1 in 333 parts of water at 15°. The author finds that *pure* acetylenecarbamide requires 1090 parts of water for solution, whilst a similar determination of the solubility of glycoluril showed a

ratio of 1 : 1060. Similar agreement was also found in the silver salts, crystalline form, &c., both compounds crystallising variously in needles, prisms, or octahedra according to the solvent employed. Glycoluril and acetylenecarbamide are therefore identical, and the author proposes the adoption of the latter name as the more suitable.

L. T. T.

Hydrocarbons from Tar-oils Boiling between 170° and 200°. By O. JACOBSEN (*Ber.*, **19**, 2511—2515).—The author has examined a sample of coal-tar oil free from thiophen, of boiling point 170—200°. By combined fractional distillation, conversion into sulphonic acids, sulphonic salts, and sulphonamides, he succeeded in isolating naphthalene, pseudocumene, hemellithene, and another hydrocarbon, boiling like the last-named at 175—175·5°, but yielding a very soluble *sulphonamide* melting at about 122—123°. On oxidation, the hydrocarbon yields an acid which crystallises in needles melting at 119—121° and volatile in steam, and also small quantities of a second acid melting at 90°. The acid of higher melting point yields isophthalic acid when oxidised with permanganate.

L. T. T.

Chloropropylbenzene. By G. ERRERA (*Gazzetta*, **16**, 310—325).—In order to determine the constitution of the chloropropylbenzene obtained by the action of chlorine on the boiling hydrocarbon, the three alcohols derivable from propylbenzene have been prepared and converted into the corresponding chloro-derivatives.

Phenylpropyl alcohol, $CH_2Ph{\cdot}CH_2{\cdot}CH_2OH$, obtained from crude storax by Rugheimer's process, is not altered by gaseous hydrogen chloride, but when heated in a sealed tube with saturated hydrochloric acid solution, it yields the chloro-derivative $CH_2Ph{\cdot}CH_2{\cdot}CH_2Cl$. This compound is a pale-yellow liquid, boiling at 219°, and resembling cymene in odour; when pure, it is very stable, being unaltered by prolonged treatment with fused zinc chloride or silver acetate. Heated with alcoholic potash, it yields phenylpropyl ethyl ether, $CH_2Ph{\cdot}CH_2{\cdot}CH_2OEt$, a colourless liquid boiling at 220°, insoluble in water.

Methyl benzyl carbinol, $CH_2Ph{\cdot}CHMe{\cdot}OH$, obtained together with allylbenzene and stilbene by the reduction of methyl benzyl ketone with sodium amalgam, is a liquid boiling at 215°, of a pale-yellow colour and agreeable odour. Heated with hydrochloric acid in sealed tubes, it yields the chloro-derivative, $CH_2Ph{\cdot}CHClMe$, a yellowish liquid, boiling at 204—207° with partial decomposition into allylbenzene and hydrogen chloride. A similar reaction occurs with alcoholic potash, metallic zinc or its chloride.

Ethyl phenyl carbinol, $CHPhEt{\cdot}OH$, prepared by prolonged reduction of the corresponding ketone with sodium amalgam, as described by Barry, is a liquid boiling at 215—217°. It is converted by gaseous hydrogen chloride, even at ordinary temperatures, into the chloride $CHPhEtCl$, a yellow liquid boiling about 200—205°, but with considerable decomposition into hydrogen chloride and allylbenzene, a change which takes place even on distillation in a vacuum. It is distinguished from the two preceding chloro-derivatives by the readiness with which it reacts with silver acetate, yielding the acetyl-

derivative, CHPhEt·OAc, a liquid boiling at 227°, of fruity odour, and insoluble in water. The chloropropylbenzene obtained by the direct chlorination of the hydrocarbon is identical with the second of the above chloro-compounds, in that it is decomposed by distillation and by alcoholic potash, as also by its stability towards silver acetate. In these properties, the chloro-derivatives of propylbenzene are directly comparable to those of ethylbenzene. V. H. V.

Reduction of Trinitro-ψ-cumene. By F. Mayer (*Ber.*, **19**, 2312—2314).—In preparing nitrocumidine by passing hydrogen sulphide through a boiling alcoholic solution of trinitro-ψ-cumene, the chief product is a new *acid*, $C_9H_{12}N_2SO_5$. It is insoluble in alcohol, ether, glacial acetic acid, &c., soluble in hot water, from which it crystallises on the addition of a few drops of hydrochloric acid in splendid, white or yellowish plates. It melts at 240° and carbonises. Salts were prepared. N. H. M.

Hemellithene. By O. Jacobsen (*Ber.*, **19**, 2517—2520).—The author has investigated this compound, which he has now isolated from the fraction of coal-tar oils boiling between 170—200° (see p. 35).

Hemellithene, $C_6H_3M_3$ [1 : 2 : 3], boils at 175—175·5°, and does not solidify at − 20°. *Tribromohemellithene*, $C_9H_9Br_3$, forms long needles melting at 245°, and is very sparingly soluble in alcohol; *trinitrohemellithene* forms prisms melting at 209°. The *monosulphonic acid* crystallises in hydrated rhombic or hexagonal plates, and yields crystalline salts; its *sulphonamide* melts at 195—196°. *Hemellithenol*, C_9H_{11}·OH [Me : Me : Me : OH = 1 : 2 : 3 : 5], is obtained by fusing the sulphonic acid with alkali. It is soluble in alcohol and ether, and crystallises in needles melting at 81°. *Hemellithylic acid*, $C_6H_3Me_2$·COOH [Me : Me : COOH = 1 : 2 : 3], is formed by the oxidation of the hydrocarbon by dilute nitric acid. It is volatile in steam, and crystallises in scales melting at 144°. Its *calcium salt* is described. Distilled with lime, it yields orthoxylene. *α - Sulphaminehemellithylic acid* [Me : Me : COOH : SO_2NH_2 = 1 : 2 : 3 : 5], is formed by the oxidation of the above sulphonamide. It melts at 238°, and with hydrochloric acid yields a *sulphohemellithylic acid* melting at 180—190°. *β-Sulphaminehemellithylic acid* [Me : Me : COOH : SO_2NH_2 = 1 : 3 : 2 : 5], formed at the same time as the α-acid, is more soluble, and melts at 174°. It yields a very soluble sulphonic acid when heated with hydrochloric acid. Both acids when fused with potash yielded an easily soluble *hydroxyhemellithylic acid*, which does not give a blue coloration with ferric chloride.

Hemellithene may be readily extracted from the tar oil by means of the sparing solubility of its barium sulphonate. L. T. T.

Reciprocal Transformations of Cymene and Cumene-derivatives. By M. Fileti (*Gazzetta*, **16**, 300—310).—In this paper are collected the hitherto observed transformations of cumene and cymene-derivatives, the one into the other, and from them is drawn the following generalisation:—A propyl-group in the para-position relatively to a carbon-atom combined with other elements or with non-oxygenated groupings, is transformed into the isopropyl-group, if this

element or grouping is displaced by an oxygenated radicle whose oxygen is directly united to the carbon-atom compound, and conversely. an isopropyl, is converted into a propyl-group when these substitutions are reversed. (Compare Widman, Abstr., 1886, 453.)

V. H. V.

Chlorocymene and Bromocymene from Thymol. By M. Fileti and F. Crosa (*Gazzetta*, **16**, 287 — 300). — Chlorocymene (parapropylmetachlorotoluene), $C_6H_3MePrCl$, is obtained almost in theoretical proportions by heating in a reflux apparatus 4 mols. of thymol with 1 mol. phosphoric chloride. On oxidation with nitric acid, Gerichten (Abstr., 1879, 238) obtained an acid, believed to be a hydrochlorocinnamic acid, $C_6H_3MeCl{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. It is here, however, shown that under these conditions three acids are formed, namely, chlorocumic, orthochloroparatoluic, and chloroterephthalic acids.

Sixty per cent. of the theoretical quantity of bromocymene, calculated according to the equation $4C_{10}H_{13}{\cdot}OH + PBr_5 = C_{10}H_{13}Br + PO(OC_{10}H_{13})_3 + 4HBr$, can be obtained by the gradual addition of 26 grams of bromine to 45 grams of phosphorus tribromide, and heating the resulting perbromide with 100 grams of thymol. On oxidation with nitric acid of sp. gr. 1·2, bromocymene yields bromocumic acid; with acid of sp. gr. 1·29, bromonitrocymene with bromocumic, bromonitrotoluic, and bromoterephthalic acids, whilst nitric acid of sp. gr. 1·39 yields the same acids without the bromonitrocymene. The bromocumic acid is identical with that obtained by the direct bromination of cumic acid; it has, therefore, the constitution $C_6H_3PrBr{\cdot}COOH$. The *bromonitrotoluic* acid crystallises in laminæ, which melt at 200° without decomposition; it is isomeric with the acid obtained by the nitration of bromotoluic acid; its *barium* salt crystallises in long, yellow needles. The bromoterephthalic acid is identical with that obtained by Fischli by the oxidation of bromoparatoluic acid.

V. H. V.

Ethylxylenes. By O. Jacobsen (*Ber.*, **19**, 2515—2516).—For the purposes of comparison with hydrocarbons obtained from the fraction of coal-tar oils boiling between 170° and 200° (this vol., p. 35), the author prepared the three isomeric ethylxylenes from the three corresponding xylenes, using Fittig's method. *Ethylorthoxylene* yields a crystalline *sulphonic acid*, giving a *sulphonamide* crystallising in needles melting at 126°. *Ethylmetaxylene* boils at 184—186°, and is still liquid at — 15°; its *sulphonic acid* is crystalline, and yields crystalline *barium* and *sodium salts;* its *sulphonamide* melts at 148°. Ethylparaxylene boils at 185°, and is still liquid at — 20°; its *sulphonic acid* crystallises in rhombic scales, forms crystalline *barium* and *sodium salts*, and yields a crystalline *sulphonamide* which melts at 117°.

L. T. T.

Ethereal Carbonates. By. G. Bender (*Ber.*, **19**, 2265—2271; compare Abstr., 1881, 48).—When naphthyl ethyl carbonate, $OC_{10}H_7{\cdot}CO{\cdot}OEt$, is boiled for some time, carbonic anhydride and alcohol are given off, and the residue consists of a mixture of α-naphthol and a compound $C_{21}H_{12}O_2$ (*loc. cit.*). The formation of

diphenylene ketone oxides from salicylic acid (Perkin, Trans., 1883, 35) and the intermolecular change of sodium phenyl carbonate to sodium salicylate, suggest that the naphthyl ethyl carbonate may have become changed to the ethyl salt, $OH\cdot C_{10}H_6\cdot COOEt$, and that 2 mols. of the latter have condensed with formation of the compound $C_{21}H_{12}O_2$; this would then be dinaphthylene ketone oxide,

$$C_{10}H_6<\begin{matrix}O\\CO\end{matrix}>C_{10}H_6.$$

The *isomeride* obtained by boiling β-dinaphthyl diethyl orthocarbonate (*loc. cit.*) crystallises from benzene in thin prisms melting at 194°.

When phenyl ethyl carbonate is heated at 300° for 3—4 hours diphenylcarbonate is formed.

Paraditolyl carbonate is obtained by heating paratolyl ethyl carbonate at 300°; it is insoluble in water, moderately soluble in hot alcohol, and melts at 115°.

Thymyl ethyl carbonate is a thick liquid boiling at 260°; at 300° it decomposes into *dithymyl carbonate*, melting at 60°.

Orthonitrophenyl ethyl carbonate is prepared by the action of ethyl chlorocarbonate on potassium orthonitrophenoxide. It is a heavy yellow oil which boils with decomposition at 275—285°. The *amido-salt*, $NH_2\cdot C_6H_4O\cdot CO.OEt$, melts at 95°; it is soluble in alcohol, moderately soluble in boiling water. When distilled, it gives off alcohol with formation of *anhydro-orthamidophenyl carbonate*, $C_7H_5NO_2$; the latter dissolves in alkalis. The *silver salt*, $C_7H_4AgNO_2$, forms an amorphous, colourless precipitate. The *ethyl salt* is obtained by boiling the compound with alcoholic potash and ethyl iodide. When heated with fuming hydrochloric acid, it yields ethyl orthamidophenol and carbonic anhydride; the constitution of the substance is therefore $C_6H_4<\begin{matrix}NEt\\-O-\end{matrix}>CO$. The *phenylhydrazine compound* of anhydro-orthamidophenyl carbonate, $C_6H_4<\begin{matrix}NH\\-O-\end{matrix}>C:N\cdot NHPh$, crystallises in yellow needles, which melt at 208°. The *acetyl-derivative* melts at 97—98°. A *mononitro-compound* was prepared; it forms long yellow needles melting at 256°. Bromine acts on the anhydro-compound with formation of a *monobromo-derivative;* this crystallises from water in plates melting at 196°. When treated with phosphoric chloride, the compound $C_7H_4ClNO_2$ is formed. N. H. M.

Parahydroxybenzyl Alcohol. By J. Biedermann (*Ber.*, **19**, 2373—2376).—*Parahydroxybenzyl alcohol*, $OH\cdot C_6H_4\cdot CH_2OH$, is prepared by dissolving parahydroxybenzaldehyde (1 part) in a mixture of water (10 parts) and alcohol (5 parts); it is then acidified with dilute sulphuric acid and gradually treated with 3 per cent. sodium amalgam (40 parts). Grey crystals of diparahydroxyhydrobenzoïn and oily drops of diparahydroxyisohydrobenzoïn separate. When hydrogen is no longer evolved, the solution is made strongly acid and left for 12 hours, it is then filtered, the filtrate extracted with ether, and the ethereal extract treated with hydrogen sodium sulphite. On evaporating the ether, the alcohol separates in needles; these are purified by dissolving them in hot chloroform and precipitating with light petroleum. It forms slender

white needles, readily soluble in water, alcohol, and ether, sparingly in benzene and chloroform; sulphuric acid dissolves it, yielding a splendid red-violet solution. It melts at 110°. The alcohol is also formed when parahydroxybenzaldehyde is kept dissolved in alcoholic potash for several weeks, but the reaction is still very incomplete. The *acetyl-derivative*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OAc$, is prepared by heating the alcohol with a mixture of glacial acetic acid and sulphuric acid. It crystallises from water in small yellow needles, melting at 84°, and is readily soluble in alcohol and ether, sparingly in water, benzene, chloroform, &c. The *diacetyl-derivative*, $OAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}OAc$, is obtained by heating parahydroxybenzyl alcohol with an excess of acetic anhydride at 160° for 5—6 hours. It forms yellowish needles melting at 75°, readily soluble in alcohol and ether, sparingly in benzene, &c.

Anisic alcohol, $OMe{\cdot}C_6H_4{\cdot}CH_2OH[=1:4]$, is formed when parahydroxybenzyl alcohol is dissolved in methyl alcohol and digested with potash and methyl iodide for some hours at 100°. The product is treated with water, heated to expel methyl alcohol and iodide, and extracted with ether. On evaporating the ether, it is obtained as an oil which gradually solidifies when kept over sulphuric acid. It crystallises from water in needles melting at 45° (compare Abstr., 1886, 460). N. H. M.

Synthesis of Betorcinol (β-Orcinol). By S. v. Kostanecki (*Ber.*, **19**, 2318—2324; compare Abstr., 1886, 242).—Paraxylorcinol $[Me_2:(OH)_2=1:4:3:5]$ was prepared from metadinitroparaxylene by replacing the nitro-groups successively by amido- and hydroxyl-groups; it is identical with Stenhouse and Groves's betorcinol (Trans., 1880, 396). The crude product obtained by nitrating paraxylene is crystallised from alcohol to remove most of the orthodinitroparaxylene, dissolved in hot alcoholic ammonia, and treated with hydrogen sulphide for about one hour; it is then evaporated to dryness. The paradinitro-compound, being more readily reduced than the meta-compound, is thus converted into paranitroparaxylidine, which is extracted by means of hydrochloric acid. The residue, insoluble in acid, was extracted with boiling alcohol, and yielded crystals of pure metadinitroparaxylene. This was reduced by dissolving in alcoholic ammonia and treating for two hours with hydrogen sulphide, and the nitroxylidine $[Me_2:NO_2:NH_2=1:4:3:5]$ so obtained was converted into the corresponding nitroxylenol. The latter crystallises in yellow plates melting at 91°. It was reduced with tin and hydrochloric acid, and the amidoparaxylenol diazotised; to 1 gram of the hydrochloride 10 grams of sulphuric acid and 100 grams of water were used, and the whole kept cold by means of ice and salt.

Paraxylorcinol so prepared has all the properties ascribed to it by Stenhouse and Groves (*loc. cit.*), except that it yields a green fluorescent solution when treated with dilute soda and chloroform.

Metaxylorcinol (Pfaff, Abstr., 1883, 918) crystallises from chloroform in white monoclinic crystals, $a:b:c=1{\cdot}7237:1:?$; $\beta=38°\ 21'$. It boils at 276—279°. When heated with sodium carbonate solution at 130°, *metaxylorcinolcarboxylic acid*, $C_6HMe_2(OH)_2{\cdot}COOH$, is formed.

The latter crystallises from dilute alcohol in well-formed prisms which melt with decomposition at 196°, and give a deep blue coloration with ferric chloride. N. H. M.

Acetalresorcinol. By — Causse (*J. Pharm.* [5], **13**, 354—358). —The author has examined the action of sulphuric acid and heat on a solution containing acetaldehyde and resorcinol. The crystals obtained are insoluble in water, ether, chloroform, and benzene. They are soluble in alcohol, which yields them again partly changed. Anhydrous ether dehydrates them, converting them into a powder, which in time aggregates to yellow, translucent crystals. Thus purified, the compound decomposes on fusing with regeneration of resorcinol. Its composition is indicated by the formula $C_{14}H_{14}O_4 = C_2H_4O + 2C_6H_6O_2 - H_2O$. The action of heat on the compound apparently removes the elements of water. Heated at 120°, a reddish powder was formed which could be obtained in large brown crystals. These had the composition $C_{28}H_{16}O_7 = 2C_{14}H_{14}O_4 - H_2O$.

The diacetyl compound, $C_{36}H_{18}O_{12}$, melts at 282°. The reactions indicate that the yellow crystals are a molecular combination of aldehyde and resorcinyl ether, $C_2H_4O_7O(C_6H_4{\cdot}OH)_2$. J. T.

Benzylamine. By T. Curtius and G. Lederer (*Ber.*, **19**, 2462—2463).—When benzaldehyde and amidoacetic acid are heated together at 130°, carbonic anhydride is evolved and benzylamine formed. Similar reactions seem to take place when cinnamaldehyde, salicylaldehyde, or orthonitrobenzaldehyde, are substituted for the benzaldehyde, but the products are not so easily isolated.

L. T. T.

Citric Acid Derivatives of Paratoluidine. By J. M. Gill (*Ber.*, **19**, 2352—2354).—*Citroparatoluidide*, $C_6H_5O_4(NH{\cdot}C_7H_7)_3$, is obtained by heating citric acid (1 mol.) and paratoluidine (3 mols.) at 140—145° for 10 hours. It crystallises from alcohol, in which it is sparingly soluble, in lustrous, microscopic needles, melting at 189°.

Citrodiparatoluide, $C_6H_5O_4(NH{\cdot}C_7H_7) : N.C_7H_7$, is formed when citric acid (1 mol.) and paratoluidine (2 mols.) are heated at 160—170° for three hours. It melts at 205°, is insoluble in water, rather readily soluble in ether and alcohol, and separates from the latter solvent in small, yellow, well-formed crystals. When heated with citric acid at 140—145°, it is converted into citroparatoluidide. Ammonia acts on it, yielding a salt of *citroparaditoluidic acid*, $C_6H_5O_4(NHC_7H_7)_2{\cdot}OH$. The latter crystallises from alcohol in groups of needles, melting at 161°. It is soluble in water, insoluble in alcohol and ether.

Citroparatoluidic acid, $C_6H_5O_4(OH) : NC_7H_7$, is prepared by adding paratoluidine (1 mol.) to a hot concentrated alcoholic solution of citric acid (1 mol.). On cooling, the solution yields clear prismatic crystals; these are heated for two hours at 160—170°, and crystallised from water. It melts at 172·5°, and dissolves readily in alcohol, ether, and hot water. N. H. M.

Azo- and Diazo-compounds. By O. Wallach (*Annalen*, **234**, 350—364).—Paracetometatoluylenediamine, obtained by the action

of acetic anhydride on metatoluylenediamine (Abstr., 1883, 329) can also be prepared by converting nitrotoluidine (m. p. 77·5°) into the aceto-compound (m. p. 144·5°), and reducing this substance with iron filings and acetic acid. By means of the diazo-reaction, the aceto-metatoluylenediamine is converted into acetamidocresol (m. p. 225°), proving that the acetyl-group occupies the para-position.

Paracetamidotolueneorthazodimethylaniline,

$$NHAc{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2,$$

is formed when a solution of the diazo-compound is poured into an ice-cold alcoholic solution of dimethylaniline. The substance crystallises in golden plates and melts at 200°. It unites with acids to form salts, which dissolve in water, yielding deep-red solutions. The acetyl-group can be eliminated by boiling with dilute sulphuric acid.

Paramidotolueneorthazodimethylaniline crystallises in golden scales. It melts at 145°, and dissolves in hot alcohol, chloroform, and benzene. The diazo-compound unites with phenol, forming *tolueneazodimethylanilineparazophenol*, $NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$.

This substance dissolves in dilute solutions of the alkalis, and is reprecipitated by carbonic acid. It also dissolves in strong acids, and is reprecipitated by the addition of water. It dissolves freely in alcohol, ether, chloroform, and benzene.

The corresponding *β-naphthol*-compound melts about 244°. It is insoluble in water, sparingly soluble in alcohol, but dissolves in strong sulphuric acid, with a red coloration.

Paracetamidotolueneorthazodiethylaniline crystallises in needles of a reddish-brown colour. It melts at 159°, and dissolves freely in alcohol, ether, chloroform, and in acids. The salts are decomposed by large quantities of water. *Orthacetometatoluylenediamine*, $NHAc{\cdot}C_6H_3Me{\cdot}NH_2$ [Me : NHAc : NH_2 = 1 : 2 : 4], prepared from orthoamidoparanitrotoluene (m. p. 107°), crystallises in white needles, and melts at 140°. It is soluble in alcohol, in ether, and in hot water. *Orthacetamidotolueneparazodimethylaniline* melts at 192°, and dissolves freely in alcohol, chloroform, benzene, and ether. *Orthamidotolueneparazodimethylaniline* melts at 215°, and is freely soluble in chloroform.

Acetamidobenzenemetazodimethylaniline, $NHAc{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2$, crystallises in plates, and melts at 184°. *Amidobenzeneazodimethylaniline* forms golden scales, soluble in alcohol, which melt at 165—166°. W. C. W.

Quinone-oximes. By J. Sutkowski (*Ber.*, **19**, 2314—2317).—When thymoquinone-oxime is dissolved in cold, fuming hydrochloric acid, a yellow precipitate is formed, consisting of dichlorothymoquinone and monochloramidothymol (Andresen, Abstr., 1881, 590). When the precipitate is boiled with glacial acetic acid, a splendid red dye is formed. The reaction is of interest, as it shows the analogy between the reactions of thymoquinone and of thymoquinone-oxime with fuming hydrochloric acid. Andresen also obtained the same products from thymoquinonechlorimide. The oxime is therefore the hydroxyl-derivative corresponding with the quinonechlorimide.

When chloramidothymol hydrochloride and chloranil are heated in glacial acetic acid solution, the red dye above mentioned is formed. Tetrachloroquinol is formed in the reaction; it crystallises in long colourless needles melting at 232°. Analyses of the dye point to the formula $C_{30}H_{35}Cl_3N_2O_3$.

In a similar manner, a dye was obtained by the action of paramidothymol on chloranil in glacial acetic acid solution. It has the composition expressed by the formula $C_{30}H_{38}N_2O_3$. It dissolves in acetic acid, alcohol, ether, and benzene, but not in water. Ammonia dissolves it with formation of a blue solution. Lead acetate gives a blue precipitate. N. H. M.

Amidine-derivatives. By M. Loeb (*Ber.*, **19**, 2340—2344).—When the compound $C_{16}H_{12}N_2Cl_2O_2$, prepared by the action of carbonyl chloride on ethenyldiphenyldiamine (Abstr., 1885, 1213), is treated with alkalis or acids, it is reconverted into the amidine. Boiling water has no action on it; boiling alcohol converts it into carbanilide, ethyl acetate, and ethyl chloride. The *ethyl salt*, OEt·CO·NPh·CMe : N·C_6H_4·COOEt, separates from its ethereal solution in hard, lustrous, rhombic crystals which melt at 90·5°. When the chloride is dissolved in benzene and treated with dry ammonia, it is converted into ethenyldiphenyldiamine and ammonium chloride; aniline acts like ammonia.

Ethenylimidobenzanilide, $CMe\langle^{N\cdot C_6H_4}_{NPh-}\rangle CO$, is prepared by the action of carbonyl chloride dissolved in benzene on an excess of ethenyldiphenyldiamine; it crystallises from benzene in large, lustrous plates melting at 118°. It is identical with the compound to which the formula $CO(C_{14}H_{13}N_2)_2$ was previously ascribed (*loc. cit.*). Dilute hydrochloric acid decomposes it with formation of aniline and phenyl cyanate.

When a saturated ethereal solution of ethenyldiphenyldiamine is treated with two or three drops of water and then with cyanogen until it has a wine-red colour, and allowed to remain for 16 hours, a black crust is formed which yields a compound, $C_{16}H_{16}N_4O$; the latter forms a white, crystalline powder very sparingly soluble in ether and benzene, and cannot be recrystallised, as it at once resinifies when heated with solvents. It becomes violet at 120°, and melts with decomposition at 165°. Its constitution is probably analogous to that of Griess' cyanocarbimidoamidobenzoic acid, as shown in the formula NPh : CMe·NPh·C(NH)CN + H_2O. Ethyl allophanate is formed when urethane (7 parts) and carbonyl chloride (1 part) are dissolved in benzene and heated at 75°. N. H. M.

Preparation of Aromatic Amides. By M. Fileti (*Gazzetta*, **16**, 281—284).—The method, proposed by Letts, for the preparation of the nitriles by heating the carboxylic acids with potassium thiocyanate, has been shown to yield the amides, if ammonium thiocyanate be substituted for the potassium salt. The former change is attributed by Kekulé to the greater dehydrating action of the potassium salt, an interpretation confirmed by the observation of

Müller that in the above method benzamide is formed if the process is conducted quickly, but phenyl nitrile if slowly. In the course of the preparation of cumonitrile, a small quantity of *cuminamide* is obtained from the crude product of the reaction, if the aqueous solution, previously rendered alkaline by ammonia, is agitated with benzene. This amide crystallises in glittering laminæ melting at 153·5°, insoluble in cold, sparingly soluble in hot water, soluble in alcohol. It is not decomposed by boiling with hydrochloric acid or potash of moderate concentration. With mercuric oxide, it yields a derivative, $(C_6H_4Pr{\cdot}CONH)_2Hg + 1\frac{1}{2}H_2O$; this crystallises in needles melting at 190°, insoluble in water, soluble in alcohol.

V. H. V.

Action of Alkyl Iodides on Dibenzylthiocarbamide. By C. Reimarus (*Ber.*, **19**, 2348—2349).—Will has shown (Abstr., 1882, 723) that alkyl iodides react with diphenyl- and dibenzyl-thiocarbamide, with formation of hydriodides of bases in which the alkyl-group is directly combined with sulphur. The author has found that the isomeric dibenzylthiocarbamide behaves analogously.

Benzylimidobenzylcarbaminethiomethyl, $SMe{\cdot}C(NHC_7H_7){:}NC_7H_7$, is formed when methyl iodide and dibenzylthiocarbamide are heated for 2—3 hours at 100°. The product is dissolved in water, treated with sodium carbonate, and extracted with ether. The *sulphate* of the base crystallises in lustrous needles readily soluble in water and alcohol; it melts at 145°. The *hydrochloride* forms large rhombic plates melting at 125°; the *hydriodide* crystallises in splendid octahedra melting at 99°, readily soluble in hot water.

Benzylimidobenzylcarbaminethioethyl, $SEt{\cdot}C(NHC_7H_7){:}NC_7H_7$, crystallises in wide prisms, apparently monoclinic, which melt at 93°; it dissolves readily in alcohol, sparingly in water. The *sulphate* forms large rhombic plates readily soluble in water and alcohol; the *platinochloride* crystallises in needles.

Corresponding compounds were also prepared from propyl iodide and amyl iodide.

N. H. M.

Phenylseleniocarbimide and Diphenylseleniocarbamide. By H. Stolte (*Ber.*, **19**, 2350—2352).—*Phenylseleniocarbimide*, CSe·NPh, is prepared by passing hydrogen selenide into aqueous soda, evaporating, and adding isocyanophenyl chloride diluted with ether to prevent the reaction becoming too violent. After a day, the product is filtered, the ether evaporated, and the residue steam-distilled and dried in a vacuum over sulphuric acid. It is a yellowish-red oil, insoluble in water, readily soluble in alcohol and ether, and has only a slight odour. When the ethereal solution of the substance is treated with ammonia, it is converted into monophenylseleniocarbamide (Abstr., 1886, 781).

Diphenylseleniocarbamide, $CSe(NHPh)_2$, is prepared from phenylseleniocarbimide by treating its ethereal solution with aniline. The product is washed with ether, and crystallised from alcohol. It melts at 186° with decomposition.

N. H. M.

Substituted Nitrogen Chlorides. By G. Bender (*Ber.*, **19**, 2272—2274).—When the compound $C_6H_4<^{NH}_{-O-}>CO$ (this vol., p. 38) is treated with bleaching powder and hydrochloric acid the *compound* $C_7H_3NO_2Cl_2$ separates in colourless needles. When the latter is brought into contact with quinol, an odour of quinone is given off, and on cooling crystals of quinhydrone separate. The compound is decomposed by alcohol, alkalis, aniline, &c., into the compound $C_6H_3Cl<^{NH}_{-O-}>CO$ (*loc. cit.*).

Acetanilide, when treated with bleaching powder in presence of acetic acid, yields the *compound* NPhCl·COMe. The latter has the properties of the compound described above. It melts at 91°; when heated to 172°, it becomes yellow, effervesces violently and is converted into its isomeride, parachloracetanilide, melting at 172°. The same change takes place when the substance is treated with cold hydrochloric acid or when warmed with absolute alcohol; if more than 2 grams be employed, a violent explosion takes place. The compound reacts with paranitraniline, yielding acetanilide and orthochloroparanitraniline.

The *compound* $<^{CH_2\cdot CO}_{CH_2\cdot CO}>NCl$ was prepared from succinimide: it crystallises from benzene in large colourless crystals melting at 148°.

Benzamide yielded the *compound* COPh·NHCl. This crystallises from water in long prisms melting at 116°. N. H. M.

Condensation of Nitrobenzaldehyde with Hydrocarbons. By O. Tschacher (*Ber.*, **19**, 2463—2464).—Baeyer has shown that fatty aldehydes, in the presence of concentrated sulphuric acid, form condensation products with aromatic hydrocarbons, whilst aromatic aldehydes do not. The author finds that the introduction of a nitro-group into the phenyl-ring gives to aromatic aldehydes the power of forming such condensation products.

With benzene, metanitrobenzaldehyde yields *metanitrotriphenylmethane*, forming crystals melting at 90°. With toluene, *metanitrophenylditolylmethane* is formed. L. T. T.

Compound of Pyruvic Acid with Hippuric Acid. By A. Hoffmann (*Ber.*, **19**, 2554—2557).—6 grams of pyruvic acid were digested with 11 grams of sodium hippurate and 25 grams of acetic anhydride on a water-bath. In a short time, a vigorous reaction takes place and the temperature of the mixture rises to 108°. The product is dissolved in alcohol, the solution diluted with water, evaporated, and the brownish crystals recrystallised from petroleum. Analyses of the compound point to the formula $C_{12}H_9NO_4$; the substance is therefore formed by the union of its two constituents (equal mols.) with elimination of the elements of water (2 mols.). It forms colourless, flat needles melting at 157°; it is very readily soluble in alcohol, ether, and acetic acid; insoluble in water. It yields salts corresponding with a bibasic acid, $C_{12}H_{11}NO_5$. The *barium salt*, $C_{12}H_9NO_5Br + 2H_2O$, was prepared; when treated with acid, it

yields the anhydride, $C_{12}H_9NO_4$, the acid not being capable of existing in the free state. When the anhydride is heated with hydrochloric acid at 140°, benzoic acid is formed. N. H. M.

Phenyliodohydracrylic Acid. By E. Erlenmeyer and J. Rosenhek (*Ber.*, **19**, 2464—2465).—*Phenyliodohydracrylic* (*α-iodo-β-phenylhydroxypropionic*) *acid*, OH·CHPh·CHI·COOH, was obtained by the action of iodine chloride on cinnamic acid. A chloriodophenylpropionic acid is probably first formed, which is then converted into the hydroxy-acid by the action of water. The acid forms large crystals which melt with decomposition at 137—139°, and are soluble in benzene. When treated with hydrochloric acid, this acid yields a compound $C_{18}H_{16}ClIO_4$, which the author believes to have the formula $CHPh:CH\cdot C(OH)<^{O}_{O}>C(OH)\cdot CHI\cdot CHClPh$. L. T. T.

Creosolcarboxylic Acid. By H. Wende (*Ber.*, **19**, 2324—2327). —*Creosolcarboxylic acid*, $OH\cdot C_6H_2Me(OMe)\cdot COOH$ [= 4 : 1 : 3 : 5], is prepared by gradually adding 4 grams of sodium to 50 grams of creosol through which a current of dry carbonic anhydride is being passed. The reaction takes place slowly with evolution of hydrogen and slight development of heat, and is assisted by gently warming; much heat is then developed, and the reaction becomes rather violent. The product, when cold, is treated with dilute hydrochloric acid, extracted with ether, and the ethereal solution extracted with sodium carbonate solution. It crystallises in needles melting at 180—182°, dissolves sparingly in water, readily in alcohol, ether, and chloroform, and is almost insoluble in benzene and light petroleum. It sublimes unchanged when carefully heated, and acquires a deep blue colour when treated with ferric chloride. The *ammonium salt* crystallises in globular groups of needles; the *potassium salt* forms small, readily soluble needles; the *barium salt* is sparingly soluble; the *copper salt* is a yellow powder; it is very electric when dry. The *methyl salt* forms small, rhombic crystals, $a : b : c = 0{\cdot}5285 : 1 : 0{\cdot}7334$; it melts at 92°, and gives a bluish-green coloration with ferric chloride. The *ethyl salt* crystallises in small needles or prisms melting at 77°.

N. H. M.

Derivatives of Opianic Acid. By C. Liebermann (*Ber.*, **19**, 2275—2287; compare Abstr., 1886, 550). — *Amidohemipinphenylhydrazide* (*azopianphenylhydrazide*), $NH<^{C:N\text{———}NPh}_{C_6H(OMe)_2\cdot CO}$, is prepared by the action of phenylhydrazine on azopianic acid. It separates from its solution in benzene in small, honey-coloured, tetragonal crystals, having a glassy lustre, $a : c = 1 : 0{\cdot}5947$. It melts at 222°, and dissolves in strong sulphuric acid and in fuming hydrochloric acid.

Amido-opianphenylhydrazide, $NH_2\cdot C_6H(OMe)_2<^{CO\cdot NPh}_{CH:N}>$, is obtained by reducing the nitro-compound (*loc. cit.*) with tin and fuming

hydrochloric acid, care being taken to prevent the reaction from becoming too violent from the heat developed. On adding water to its alcoholic solution, it crystallises in slender needles melting at 137—143°.

Normethylnitro-opianphenylhydrazide,

$$NO_2{\cdot}C_6H(OH)(OMe)<\begin{matrix}CO{\cdot}NPh\\ -CH:N-\end{matrix}>,$$

is formed when nitro-opianphenylhydrazide is boiled with alcoholic potash, and the potassium salt thus obtained treated with hydrochloric acid. It crystallises in yellow, glittering, rhombic plates melting at 191°. The *potassium salt* is a carmine-red powder.

Opianoxime anhydride (*hemipinimide*), $C_{10}H_9NO_4$, is prepared by boiling opianic acid (1 mol.) dissolved in nine times its weight of 80 per cent. alcohol with hydroxylamine hydrochloride ($1\frac{1}{4}$ mol.) for two to three hours. It crystallises from alcohol in long, very slender needles melting at 228—230°. An aqueous or alcoholic solution containing only a trace of the substance has a fine blue fluorescence. It sublimes unchanged, and can be heated with strong sulphuric acid without decomposition. Cold aqueous alkali dissolves it, forming a yellow solution which soon becomes colourless. When heated with alkali, it yields hemipinic acid and ammonia. The compound was also prepared by heating ammonium hemipinate. The *potassium salt*, $C_{10}H_8ONK$, is a white compound almost insoluble in cold absolute alcohol. The *silver salt* was also prepared.

Hemipinethylimide, $C_{10}H_8O_4:NEt$, is obtained by heating potassium hemipinimide with ethyl iodide at 150°. It crystallises from boiling water in colourless needles resembling hemipinimide; the solution shows the same fluorescence. It dissolves very readily in alcohol, acetone, and benzene, and melts at 96—98°.

The formation of hemipinimide is interesting on account of its complete analogy with observations lately made in the phthalic acid series. The author assigns to the compounds phthalimide and hemipinimide the respective constitutional formulæ $CO<\begin{matrix}-O-\\ C_6H_4\end{matrix}>C:NH$ and $CO<\begin{matrix}\overline{\quad}O\overline{\quad}\\ C_6H_2(OMe)_2\end{matrix}>C:NH$.

Anilido-opianic acid, $C_{16}H_{15}NO_4$, is obtained by boiling a solution of equal weights of opianic acid and aniline, dissolved in glacial acetic acid, for 10 minutes. On cooling, the whole solidifies to a white mass, which is washed with water, dissolved in benzene, and precipitated with ether. It melts at 186—187°. It dissolves only in strong alkali solution. *Anilidonitropianic acid*, $C_{16}H_{14}N_2O_6$, is prepared from nitropianic acid in a manner similar to the above compound. It crystallises in needles melting at 183—184°. When treated with alkali, it yields a sparingly soluble *potassium salt*.

Nitrohemipinic acid, $NO_2{\cdot}C_6H(OMe)_2(COOH)_2$, is very readily prepared by boiling nitropianic acid with fuming nitric acid (4 parts) for one hour. It melts at 166° (not 155°), but has all the other properties ascribed to it by Prinz (Abstr., 1882, 402). When heated above its melting point, it gives up water and yields a yellowish compound, probably the anhydride.

Opianic anhydride, $[CHO{\cdot}C_6H_2(OMe)_2{\cdot}CO]_2O$, is formed when opianic acid is heated at 160° in a current of dry air. It crystallises well from acetone and melts at 234°. It is identical with the compound described by Wegscheider (Abstr., 1883, 996) as triopiamide, $C_{30}H_{28}O_{14}$. When boiled with alkali, it is gradually transformed into opianic acid. Strong nitric acid converts it into nitropianic acid.

N. H. M.

Opianic Acid Derivatives. By C. Liebermann and S. Kleemann (*Ber.*, **19**, 2287—2299).—*Acetylopianic acid*,

$$<\begin{matrix}CO\text{———}O\\C_6H_2(OMe)_2\end{matrix}>CH{\cdot}OAc,$$

is prepared by heating opianic acid and dry sodium acetate with acetic anhydride. The excess of acetic anhydride is then removed by contact with cold water for 24 hours, and the remaining compound crystallised from boiling water. It melts at 120—121°. It is insoluble in cold aqueous alkali, and when boiled with it, is decomposed into opianic and acetic acids.

Acetylnitropianic acid, $<\begin{matrix}CO\text{———}O\\C_6H(NO_2)(OMe)_2\end{matrix}>CH{\cdot}OAc$, is prepared in a manner similar to acetylopianic acid. It is a yellow substance insoluble in cold sodium carbonate solution.

Propionylopianic acid, $C_{13}H_{14}O_6$, crystallises in needles melting at 111°.

Anhydracetamidohemipinic acid, $C_{10}H_8AcNO_5$, and the *propionyl-compound*, $C_{10}H_8(C_3H_5O)NO_5$, melt at 164° and 139° respectively; they are very unstable.

Meconine-acetic acid, $<\begin{matrix}CO\text{———}O\\C_6H_2(OMe)_2\end{matrix}>CH{\cdot}CH_2{\cdot}COOH$, is obtained by heating opianic acid (3 parts), malonic acid (1½ part), glacial acetic acid (2 parts), and sodium acetate (1½ part) for five hours at 100°; the colourless, crystalline product is crystallised from water. It forms lustrous needles melting at 167°; it has an acid reaction and dissolves in ammonia. The *silver*, *calcium*, &c., *salts* were prepared. The *ethyl salt* crystallises in plates soluble in alcohol, ether, and hot water; it melts at 82·5°. The reactions of the acid are analogous to those of phthalylacetic acid. When boiled with baryta, and the excess of baryta afterwards removed by means of carbonic anhydride, *barium opianylacetate** is obtained; it forms lustrous prisms. The free acid is not capable of existence. When the silver salt is treated with methyl iodide, it yields, not methyl opianylacetate, but *methyl meconine-acetate;* the latter crystallises in lustrous plates melting at 124°.

Normeconine-acetic acid, $<\begin{matrix}CO\text{———}O\\C_6H_2(OH)_2\end{matrix}>CH{\cdot}CH_2{\cdot}COOH$, is prepared by heating meconine-acetic acid with hydriodic acid and phosphorus; the product is diluted with water and filtered. It crystallises from water in long plates melting at 228°. The *calcium* and *barium salts* form white crystalline precipitates. When the acid is

* The formula and analysis given in the original do not agree.

heated with ferric chloride, it acquires a characteristic blue colour, which changes to green in presence of an excess of ferric chloride. The *ethyl salt* separates from its solution in boiling water as an oil, which then solidifies and melts at 131°. Its solution is fluorescent and reduces silver solution, but to a smaller extent than the free acid. It has an acid reaction and precipitates from baryta solution a yellow barium salt of the ether. This acid property and the power of reducing silver solutions is due to the presence of pyrocatechol-hydroxyl.

Orthonitromeconine-acetic acid,

$$<\begin{matrix}CO\text{———}O\\C_6H(NO_2)(OMe)_2\end{matrix}>CH\cdot CH_2\cdot COOH\ [NO_2 : CH\cdot CH_2\cdot COOH = 1 : 2],$$

is obtained by dissolving meconine-acetic acid in fuming nitric acid and afterwards precipitating with water. It forms colourless crystals melting at 176°. The *calcium salt* forms yellow needles. The *ethyl salt* crystallises in lustrous needles, readily soluble in alcohol and benzene; it melts at 129°. Nitromeconine-acetic acid dissolves in sulphuric acid, forming a yellow solution; this, when warmed, acquires a cherry-red colour, characteristic of compounds containing a nitro-group in the ortho-position to a long side-chain (Baeyer, Abstr., 1882, 620). When the nitro-compound is reduced with tin and hydrochloric acid, *dimethoxyhydrocarbostyril-lactone*,

$$<\begin{matrix}CO\text{———}O\\C_6H(OMe)_2\end{matrix}>\begin{matrix}CH\cdot CH\\NH\cdot CO\end{matrix}>,$$

is formed. This crystallises from water in colourless needles, melting with evolution of carbonic anhydride at 256°. It is readily soluble in alcohol and glacial acetic acid, insoluble in ether and benzene. It dissolves in baryta; when the solution is boiled and treated with carbonic anhydride and evaporated down, lustrous needles of barium dimethoxyhydrocarbostyrilcarboxylate are obtained.

Dimethoxydihydrochloroquinoline lactone, $C_{12}H_{10}NClO_4$, is prepared by heating the lactone just described with phosphorus pentachloride and some phosphorus oxychloride for two hours at 165—170°; the product is poured into iced water, and the precipitate crystallised from alcohol, from which it separates in needles; these melt at 218° with evolution of carbonic anhydride. The *barium salt*, obtained by boiling the lactone with baryta, and the *silver salt* were prepared.

Dihydroxydihydroquinoline lactone, $C_{10}H_7NO_4$, is obtained by heating the above chloro-derivative dissolved in glacial acetic acid for one hour at 120° with hydriodic acid. It melts at 220° with decomposition.

N. H. M.

Azo-opianic Acid. By H. Grüne (*Ber.*, **19**, 2299—2305).—Azo-opianic acid, prepared from nitropianic acid, melts at 200° with decomposition (not 184° as given by Prinz, Abstr., 1882, 404). The *potassium salt* is a white crystalline powder. The *ethyl salt* crystallises in needles melting at 98°; the *methyl salt* melts at 127°. The author confirms the statement of Prinz (*loc. cit.*) that azopianic acid, when boiled with baryta in excess, yields barium amidohemipinate

The yield is almost quantitative. *Sodium amidohemipinate* crystallises from alcohol with 3 mols. H_2O, in long, almost white needles; it is very readily soluble in water. The *copper salt* (with 7 mols. H_2O) crystallises in stellate groups of slender, green needles. The aqueous solution of the free acid has a fine green fluorescence which disappears when alkalis or acids (except acetic acid) are added. It reduces a cold ammoniacal silver solution, and Fehling's solution when warmed.

Anhydrodiazohemipinic acid, $COOH{\cdot}C_6H(OMe)_2{<}\overset{N_2{\cdot}O}{CO}{>}$, is obtained when a cooled solution of sodium amido-hemipinate is treated with sodium nitrate and hydrochloric acid. It is a bright yellow, microcrystalline powder which becomes superficially red when exposed to light, and explodes at 140—150° or when struck. It dissolves readily in alkalis and acids; when boiled with water, it gives off nitrogen and yields a hydroxy-acid, which gives an intense blue-violet colour with ferric chloride. The *hydrochloride*, $COOH{\cdot}C_6H(OMe)_2(COOH){\cdot}N_2Cl + H_2O$, crystallises in long, colourless needles; in presence of water, it decomposes into hydrochloric acid and free anhydroazohemipinic acid. When the diazohemipinic acid is boiled with alcohol under slight pressure, it is converted, with evolution of nitrogen, into hemipinic acid.

Nitrohemipinic acid was prepared by Liebermann's method (this vol., p. 46). The *potassium salt* crystallises in deep yellow prisms, readily soluble in water and alcohol, the *silver salt* is also yellow.

Nitrohemipinic anhydride, $NO_2{\cdot}C_6H(OMe)_2{<}\overset{CO}{CO}{>}O$, is prepared by heating the acid at 160—165° for two hours; it crystallises from benzene in bright yellow prisms melting at 145°. When nitrohemipinic acid is reduced with ferrous sulphate and soda, amidohemipinic acid is formed identical with the acid obtained by boiling azo-opianic acid with baryta.

The results of the experiments above described confirm the view brought forward by Liebermann (*loc cit.*) that Prinz's so-called azo-opianic acid is not an azo-derivative of opianic acid but an internal anhydride of orthamidohemipinic acid.

When nitrohemipinic acid is reduced with tin and hydrochloric acid, the *compound* $COOH.C_6H_2(OMe)_2{\cdot}NH_2,HCl$ is formed.

N. H. M.

Derivatives of Normethylnitropianic Acid. By K. Elbel (*Ber.*, **19**, 2306—2312).—Normethylnitropianic acid

$$COH{\cdot}C_6H(COOH)(OH)(OMe){\cdot}NO_2,$$

is best prepared by heating finely powdered nitropianic acid with fuming hydrochloric acid (10 parts) for 15 hours at 100°, with a reflux condenser, hydrogen chloride being passed in all the time. The product is evaporated down, when the normethyl-compound separates; the yield is 80 per cent. of the theoretical.

Normethylorthanhydramidohemipinic acid (normethylazo-opianic acid), $OMe{\cdot}C_6H(OH)(COOH){<}\overset{CO}{NH}{>}$ [OMe : OH : COOH : CO : NH = 4 : 3 : 2 : 1 : 6], is obtained by treating a boiling saturated aqueous

solution of normethylnitropianic acid with tin and hydrochloric acid. It is dissolved in alcohol and precipitated with water. It crystallises in colourless, lustrous needles which melt at 174—175° with decomposition; it is readily soluble in alcohol, sparingly in benzene, and insoluble in ether. When boiled with baryta, crystals of barium normethylamidohemipinate are formed. The *diacetyl*-derivative, $OMe{\cdot}C_6H(OAc)(COOH){<}^{\cdot CO\cdot}_{NAc}{>}$, is obtained by boiling normethylanhydramidohemipinic acid with sodium acetate and acetic anhydride (10 parts) for one hour. It melts at 205°, dissolves readily in benzene; the alcoholic solution has a fine blue fluorescence. It is very unstable and changes when kept into the *monacetyl* compound, $OMe{\cdot}C_6H(OAc)(COOH){<}^{CO}_{NH}{>}$, melting at 198°.

Normethylnitropianic acid phenylhydrazine crystallises in red needles which melt at 178—179° with decomposition. When boiled with glacial acetic acid, it parts with the elements of water and yields *normethylnitropiazide*, $NO_2{\cdot}C_6H(OMe)(OH){<}^{CO{\cdot}NPh}_{CH:N-}{>}$. The latter crystallises in lustrous, lemon-coloured, rhombic plates melting at 191°. It dissolves unchanged in dilute potash solution. The *potassium salt* is very readily soluble in water, almost insoluble in absolute alcohol. *Normethylamido-opiazide* is obtained by boiling the nitro-compound suspended in ammonia with ferrous sulphate. It crystallises from alcohol in short, almost colourless prisms.

Normethylnitropianoximic acid,

$$NO_2{\cdot}C_6H(OMe)(OH)(COOH){\cdot}CH:NOH \quad [= 6:4:3:2:1],$$

is formed by mixing a boiling solution of normethylnitropianic acid in water (40 parts) with an aqueous solution of hydroxylamine hydrochloride and sodium acetate. It crystallises from alcohol in lustrous yellow needles which become brown when warmed, and melt at 252°. It has a slight reducing action on Fehling's solution. It dissolves in alkali with a deep-red colour, and the solution gives off ammonia when boiled, with formation of *normethylnitrohemipinic acid*, $NO_2{\cdot}C_6H(OMe)(OH)(COOH)_2$ [= 6 : 4 : 3 : 2 : 1]. The latter crystallises from alcohol in almost white, silky needles, readily soluble in water and alcohol; it melts at 220°. The *hydrogen potassium salt* forms bright yellow prisms. The same acid is formed when normethylhemipinic acid is nitrated with dilute nitric acid.

Normethylnitrohemipinimide, $NO_2{\cdot}C_6H(OMe)(OH){<}^{\cdot CO{\cdot}O\cdot}_{C(NH)}{>}$, is obtained by boiling an alcoholic solution of normethylnitropianic acid with hydroxylamine hydrochloride, or better by boiling normethylnitropianoximic acid with glacial acetic acid. It crystallises in bright yellow needles which melt at 252° with decomposition.

N. H. M.

Homo-orthophthalimide. By S. Gabriel (*Ber.*, **19**, 2363—2367; compare Abstr., 1886, 812, and this vol., p. 61).—When a solution of homo-orthophthalimide (2 grams) and potash (1 gram) in methyl alcohol (15 c.c.) is digested with methyl iodide (4 grams) at 100°,

dimethylhomo-orthophthalimide, $C_6H_5Me_2NO_2$, is formed. The latter crystallises from water in flat needles melting at 119—120°; it is readily soluble in the usual solvents and in alkali. When heated with potash and methyl iodide at 100°, it yields the *trimethyl-derivative*, $C_6H_4Me_3NO_2$; this crystallises in long needles melting at 102—103°; it is readily soluble. Alkali does not dissolve it.

Homo-orthophthalmethylimide, $C_6H_4<\begin{matrix}CH_2\cdot CO\\CO\cdot NMe\end{matrix}>$, is formed by evaporating a mixture of homo-orthophthalic acid and methylamine, and distilling the residue. It forms long, colourless needles, which melt at 123° and boil at 314—318°. It is readily soluble in the usual solvents and dissolves in alkalis. When heated with methyl iodide and potash, it yields trimethylhomophthalimide melting at 102—103°. In the latter compound, therefore, one of the methyl-groups is attached to nitrogen. Trimethylhomophthalimide is hardly attacked by fuming hydrochloric acid at 100°, and so cannot contain methoxyl; when heated with the fuming acid at 230—240°, the *anhydride* of a bibasic acid, $C_7H_4Me_2<\begin{matrix}CO\\CO\end{matrix}>O$, is obtained. This crystallises in flat crystals melting at 82·5—83°; the *silver salt*, $C_{11}H_{16}O_4Ag_2$, was prepared. The anhydride is also formed when dimethylhomophthalide (from homophthalide, potash, and methyl iodide) is heated at 230° with fuming hydrochloric acid; ammonia is formed in the reaction.

Tri- and di-methylhomophthalimide and the anhydride (m. p. 82·5—83°) have probably the constitution expressed in the formulæ—

$$C_6H_4<\begin{matrix}CMe_2\cdot CO\\CO\cdot NMe\end{matrix}>,\quad C_6H_4<\begin{matrix}CMe_2\cdot CO\\-CO\cdot NH-\end{matrix}>,\text{ and }C_6H_4<\begin{matrix}CMe_2\cdot CO\\CO\text{——}O\end{matrix}>.$$

N. H. M.

Action of Amines on Phthalylacetic Acid. By E. Mertens (*Ber.*, **19**, 2367—2373).—Pure phthalylacetic acid is stirred with water and treated with a 33 per cent. solution of ethylamine until it is dissolved; it is then filtered and saturated with hydrogen chloride, being kept cold the whole time. A white crystalline substance gradually separates with slight evolution of carbonic anhydride. Analyses show the compound to have the formula $C_{23}H_{24}O_5N_2$. It melts at 129°, dissolves readily in warm alcohol, ether, and chloroform, more sparingly in benzene; boiling water decomposes it.

Methylenephthalethimidine, $CO<\begin{matrix}C_6H_4\\NEt\end{matrix}>C:CH_2$, is formed when the compound $C_{23}H_{24}O_5N_2$ is heated above its melting point; carbonic anhydride and water are evolved. It has a carrot-like odour, distils with steam, and is readily soluble in alcohol, ether, and chloroform, &c. It strongly resembles Gabriel's methylenephthalomethimidine (Abstr., 1885, 1228).

Phthalethimidylacetic acid, $CO<\begin{matrix}C_6H_4\\NEt\end{matrix}>C:CH\cdot COOH$, is obtained by keeping a solution of the compound $C_{23}H_{24}N_2O_5$ in sulphuric acid (10 parts) for 24 hours, and then pouring it into water. The white crystalline precipitate is crystallised from dilute alcohol, from which it

separates in yellow needles melting at 180° with effervescence. It is readily soluble in hot water, alcohol, and ether, less soluble in benzene. The *silver salt* forms a flaky crystalline precipitate; the *barium salt* crystallises in yellow lustrous needles. Propylamine and phthalylacetic acid yield the *compound* $C_{25}H_{28}O_5N_2$. It forms large well-formed prismatic crystals which melt with effervescence at 103°. It behaves similarly to the ethylamine compound.

Acetophenone-orthocarboxanilide, $COMe\cdot C_6H_4\cdot CO\cdot NHPh$, is obtained by warming phthalylacetic acid with aniline. After the evolution of carbonic anhydride has ceased, the whole is left for 24 hours, when the substance separates in white crystals. It crystallises from benzene in large, well-formed cubes which melt at 189—192°, and dissolve readily in warm alcohol, ether, or chloroform. When heated at 204° and afterwards at 230°, it is converted with evolution of aniline and water into *methylenephthalphenimidine*, $CO<^{C_6H_4}_{NPh}>C:CH_2$. The latter crystallises in yellowish prisms readily soluble in alcohol, ether, and chloroform; it melts at 100°. When acetophenonecarboxanilide is kept dissolved in strong sulsulphuric acid for 24 hours, it is converted into a *compound*, $C_{15}H_{11}NO$, isomeric with the compound just described. It is sparingly soluble in alcohol and ether, readily in benzene, chloroform, and light petroleum; it melts at 265°. N. H. M.

Bromoterephthalic Acid. By M. Fileti (*Gazzetta*, **16**, 284—287).—Fischli (Abstr., 1879, 639) states that the monobromoterephthalic acid obtained by the oxidation of bromotoluic acid retains 1 mol. H_2O, even after drying at 120°. As the same acid obtained from bromocymene was found to be anhydrous, the author has repeated Fischli's experiments. The analytical results obtained for the proportion of carbon and bromine show that this acid is also anhydrous. It melts at 296°, and at the same time sublimes. Its *silver salt* is precipitated as a white, gelatinous mass, somewhat soluble in water. The *methyl salt*, $C_6H_3Br(COOMe)_2$, obtained from the said chloride (Fischli), as also from the acid itself (Fileti), crystallises in acicular prisms, melting at 52°; it presents a well-marked chromatic polarisation. V. H. V.

Cumidic Acids. By E. Schnapauff (*Ber.*, **19**, 2508—2511).—The author prepared *α-cumidic acid*,

$$C_6H_2Me_2(COOH)_2\ [Me:Me:COOH:COOH = 1:3:4:6],$$

by a modification of Wurtz's process, by the action of ethyl chlorocarbonate and sodium amalgam on dibromometaxylene. This acid forms glittering prisms melting much above 320°, and subliming with only slight decomposition. It is easily soluble in boiling alcohol, very sparingly in boiling water. Its *barium salt* crystallises with $1\frac{1}{2}$ mol. H_2O, and is very soluble in water: the *methyl salt* forms long needles or plates and melts at 76°.

Cumidic acid, obtained as described by Jannasch (this Journal, 1871, 240) by the oxidation of durene, was converted into the methyl

salt, and this by crystallisation from alcohol was separated into two parts, the one melting at 76° the other crystallising in needles and melting at 114°. The former was the methyl salt of the α-acid just described. The ether melting at 114° yielded *β-cumidic acid* [Me : Me : COOH : COOH = 1 : 4 : 2 : 5] on hydrolysis. This acid is easily soluble in boiling alcohol, very sparingly in boiling water; it crystallises in hexagonal prisms, and sublimes at high temperatures without previous fusion. Its *barium salt* crystallises with $2\frac{1}{2}$ mols. H_2O; its *methyl salt* melts at 114° and boils at about 297° (corr.). When the barium salt is distilled with excess of lime, paraxylene is formed, so that the above formula may be regarded as established.

Jannasch's acid is, therefore, a mixture of two isomeric cumidic acids. L. T. T.

Reaction of Stilbene. By G. Errera (*Gazzetta*, **16**, 325).—Kade (Abstr., 1880, 46) states that stilbene in alcoholic solution gives a red coloration when heated with a solution of ferric chloride. It is here shown that this change is in reality due to the presence of water in the alcohol, which causes a partial decomposition of the ferric chloride into hydrochloric acid and some stable form of ferric hydroxide. Stilbene is not even necessary for the reaction; if absolute alcohol is used no colour-change ensues. V. H. V.

β-Naphthaquinone. By T. Zincke (*Ber.*, **19**, 2493—2502).—In the hope of elucidating the constitution of the two compounds, $C_{32}H_{18}N_4O_6$ and $C_{34}H_{22}N_4O_6$ (Abstr., 1882, 736, and 1883, 210), obtained by the action of nitrous acid on β-naphthaquinone-anilide and -toluide respectively, the author has undertaken similar investigations with phenanthraquinone. In the present communication, the author details some preliminary experiments as to the action of alkalis on halogen-derivatives of β-naphthaquinone, which were made to determine whether β-naphthaquinone-derivatives undergo changes similar to the conversion, by the action of alkalis, of phenanthraquinone into diphenyleneglycollic acid.

Bromo-β-naphthaquinone, [O : O : Br = 1 : 2 : 3], obtained by the action of bromine in acetic solution on β-naphthaquinone, and crystallising in red prisms melting at 177—178°, dissolves readily in cold dilute alkalis. From these solutions, acids precipitate hydroxybromo-β-naphthaquinone, described by Merz and Baltzer. Aniline and ammonia also act on bromo-β-naphthaquinone, forming compounds analogous to naphthaquinoneanilide. *Dibromo-β-naphthaquinone*, [O : O : Br : Br = 1 : 2 : 3 : 4], could not be obtained directly from naphthaquinone, but was formed by the action of excess of bromine on an acetic solution of the monobromo-derivative. It is best obtained, however, by the action of bromine on α-amido-β-naphthol. It crystallises in red, rhombic scales or tables, sparingly soluble in alcohol and ether, and melts at 172—174°. With ammonia and aniline, it yields the same compounds as the monobromo-derivative. It dissolves in cold dilute alkalis, and from these solutions acids precipitate a substance, crystallising in small white needles; this has not been further investigated.

Chloro-β-naphthaquinone, [O : O : Cl = 1 : 2 : 3], is formed when chlorine is passed through a solution of β-naphthaquinone in ten times its weight of glacial acetic acid, until a precipitate begins to be formed. It crystallises in red needles, soluble in alcohol, glacial acetic acid, and benzene, and melts at 172°. It gives an additive product with hydrochloric acid which forms white crystals. It dissolves in dilute alkalis, and this solution when acidified yields hydroxychloro-α-naphthaquinone. The unstable β-hydroxy-compound undoubtedly first formed passes into the more stable α-derivative. When chloro-β-naphthaquinone is reduced with sulphurous acid in acetic solution, *chloro-β-naphthaquinol*, $C_6H_5Cl(OH)_2$, is formed, and crystallises in long, colourless needles melting at 116—117°. The *anilide* and *imide* of chloro-β-naphthaquinone both crystallise in dark-coloured scales having a metallic lustre, the former substance melting at 253°, the latter at 260°.

Dichloro-β-naphthaquinone, [O : O : Cl : Cl = 1 : 2 : 3 : 4], may be obtained directly from the quinone, but is best prepared by the action of chlorine on α-amido-β-naphthol. It crystallises in red scales, needles, or tables, easily soluble in chloroform and boiling benzene, sparingly in alcohol, melts at 184°, and sublimes without decomposition. With ammonia or aniline, it forms the imide or anilide respectively. When reduced with sulphurous acid in acetic solution, it yields dichloro-β-naphthaquinone, crystallising in white needles which melt at 125°. It dissolves in cold dilute alkali, and this solution when heated becomes cloudy, and deposits a greyish-white precipitate. If the cold alkaline solution be treated with excess of acid, an acid of the formula $C_{10}H_6Cl_2O_3$ is liberated. This acid crystallises with 1 mol. H_2O in small white needles, melts at 98—100°, and is easily soluble in alcohol, sparingly so in water. Its *methyl salt* forms colourless scales or hexagonal plates melting at 137—138°. The action of the alkali on the dichloroquinone appears to take place according to the equation $C_{10}H_4Cl_2O_2 + H_2O = C_{10}H_6Cl_2O_3$. The author considers the action to be similar to the action of alkalis on phenanthraquinone, and the most probable constitution of the acid to be $CCl\ll^{C_6H_4}_{CCl-}>C(OH)\cdot COOH$. The acid forms an *acetyl-derivative*, melting at 75—76°. Boiling baryta-water or alkalis cause a separation of carbonic anhydride. When a solution of the acid in glacial acetic acid is treated with concentrated sulphuric acid at 120°, hydrogen chloride is evolved, and a yellow crystalline compound melting at 224—226° is produced. The acid is decomposed on heating its aqueous solution, a yellow compound of intense odour and volatile in steam being amongst the products of reaction.

The experiments on the bromo-derivatives were carried out in conjunction with Weltner, those on the chloro-derivatives with C. Fröhlich. L. T. T.

Benzene- and Toluene-azonaphthols and their Isomeric Hydrazine-derivatives. By T. Zincke and F. Rathgen (*Ber.*, **19**, 2482—2493).—When the two position-isomerides, benzeneazo-β-naphthol and β-naphthaquinonehydrazide (see Zincke and Bindewald,

Abstr., 1885, 391), are reduced by means of stannous chloride, the former yields α-amido-β-naphthol, the latter β-amido-α-naphthol. When α-amido-β-naphthol is oxidised, β-naphthaquinone is formed, but the authors find that β-amido-α-naphthol yields under similar conditions β - dinaphthaquinone (β - dinaphthadiquinone). Both quinones yield with bromine dibromo-β-naphthaquinone.

When heated with nitric acid, benzeneazo-β-naphthol yields dinitro-β-naphthol, $C_{10}H_5(OH)(NO_2)_2$ [$NO_2 : OH : NO_2 = 1 : 2 : 4$], whilst β-naphthaquinonehydrazide yields dinitro-α-naphthol [$OH : NO_2 : NO_2 = 1 : 2 : 4$]. The β-derivative melts at 194°, the α- at 138°. When the above isomeric hydrazide and azo-compound are reduced in alkaline solution, they are both decomposed into aniline and amido-naphthol.

The author disputes the correctness of Denaro's assertion (Abstr., 1886, 246) that two isomeric benzeneazonaphthols can be obtained from β-naphthol.

The authors have also investigated the corresponding toluene-derivatives. *Paratolueneazo-α-naphthol*, $OH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_7H_7$ [$OH : N_2 = 1 : 4$], was prepared like the similar benzene-compound. It crystallises in dark-red flakes having a metallic lustre, and melts with decomposition at 208°. It is easily soluble in acetone, aniline, and alkalis, sparingly so in alcohol and acetic acid. No bromo-derivative could be obtained. Nitric acid yields dinitro-α-naphthol (b. p. 139°). The *hydrochloride* and *hydrobromide* form bluish-green scales, which are slowly decomposed by water, rapidly by alcohol. It also forms metallic derivatives. The *ethoxide* crystallises in red needles, which appear yellow by transmitted light, and melt at 126—127°; the *methoxide* melts at 103—104°; the *acetyl-derivative* crystallises in yellow needles melting at 101—102°. *Orthotolueneazo-α-naphthol*, [$OH : N_2 = 1 : 4$], forms red needles melting at 144—146°, soluble in alcohol, benzene, and acetic acid. It forms dinitro-α-naphthol with nitric acid, and yields salts resembling those of the para-compound. The *ethoxide* crystallises in red scales melting at 94°, the *methoxide* in reddish-brown needles melting at 93°. Para- and ortho-tolylhydrazides of α-naphthaquinone are identical with the corresponding azo-compounds.

Paratoluene-β-naphthol, $C_{10}H_6O{\cdot}N_2H{\cdot}C_7H_7$, or $C_{10}H_6(OH){\cdot}N_2{\cdot}C_7H_7$ [$O : N_2 :: 2 : 1$], forms red crystals with green fluorescence, is soluble in alcohol, benzene, and acetone, and melts at 134—135°. It forms very unstable salts with acids. The *dibromo-derivative* forms intensely red needles melting at 190°. Nitric acid converts the azo-compound into dinitro-β-naphthol (m. p. 194°). *Orthotolueneazo-β-naphthol*, [$O : N_2 = 2 : 1$], crystallises in small red needles or scales which melt at 131°. With nitric acid, it yields a dinitro-β-naphthol melting at 167°. The tolylhydrazides of β-naphthaquinone are, like the similar phenylhydrazide, isomeric and not identical with the azo-compounds. They resemble them, however, very closely, the chief difference being their greater solubility in alkalis. *β-Naphthaquinone-paratolylhydrazide*, $C_{10}H_6O{\cdot}N_2H{\cdot}C_7H_7$ [$O : N_2 = 1 : 2$], crystallises in small, red, glistening needles which melt at 145°. The *dibromo-derivative*, $C_{17}H_{12}Br_2O$, forms red, sparingly soluble needles melting at 236°. *β-Naphthaquinone-orthotolylhydrazide* crystallises in red scales with a

golden-yellow fluorescence. It is easily soluble in the usual solvents and melts at 156°. Its *dibromo-derivative* melts at 254°. Besides these hydrazides, the product of the action of the tolylhydrazine on the β-naphthaquinone always contained considerable quantities of dinaphthyldiquinol. L. T. T.

New Diamidodinaphthyl. By P. Julius (*Ber.*, **19**, 2549—2552).—αα-Dinaphthyl is best prepared by distilling β-dinaphthol with zinc-dust (10—15 parts): the distillate is re-distilled in a vacuum and recrystallised from glacial acetic acid.

Mononitrodinaphthyl, $C_{10}H_7 \cdot C_{10}H_6 \cdot NO_2$, is obtained by adding nitric acid, of sp. gr. 1·3 (20 grams), to a solution of dinaphthyl (10 grams) in 150 c.c. of glacial acetic acid. It crystallises in lustrous, orange-coloured plates melting at 188°. It dissolves easily in hot benzene and glacial acetic acid, less readily in alcohol and ether.

Dinitrodinaphthyl, $NO_2 \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot NO_2$, is prepared by treating a solution of 10 grams of dinaphthyl in 150 c.c. of glacial acetic acid with 80 grams of nitric acid, and then heating at 60°. It crystallises in bright yellow, voluminous needles which melt at 280°, it dissolves very sparingly in benzene, xylene, and glacial acetic acid, and is practically insoluble in other solvents.

Diamidodinaphthyl hydrochloride, $NH_2 \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot NH_2, 2HCl$, is prepared by treating 10 grams of the dinitro-compound, suspended in 200 c.c. of glacial acetic acid, with hydrochloric acid, and 50 grams of zinc-dust. It is readily soluble in water, sparingly in strong hydrochloric acid; when exposed to the air, it quickly becomes green. The free base could not be isolated. The *diacetyl-derivative* crystallises in almost colourless needles which melt above 300°; it is insoluble. When the hydrochloride is treated with ferric chloride, dark-brown, lustrous needles of *diimidodinaphthyl hydrochloride*, $C_{20}H_{16}N_2Cl_2$, are obtained; this is reconverted by reducing agents into the diamido-compound. N. H. M.

Tetrahydroxyanthraquinones. By E. Noah (*Ber.*, **19**, 2337—2340).—When metahydroxybenzoic and gallic acids (equal mols.) are heated with sulphuric acid (10 parts) for 20 hours at 170°, two *tetrahydroxyanthraquinones*, $C_{14}H_4(OH)_4O_2$, are formed, together with hexahydroxyanthraquinone. The product is extracted with alcohol, the solution evaporated to dryness, and the residue extracted with benzene. The solution contains now only one tetrahydroxyanthraquinone. This crystallises in long, slender, red, lustrous needles, which do not melt at 350°, and sublime with difficulty, becoming partly carbonised. It is readily soluble in alcohol, acetone, and glacial acetic acid, sparingly in benzene, xylene, &c. The solutions in sulphuric acid and in caustic alkali are violet and emerald coloured respectively. The *tetracetyl-derivative* crystallises in yellow microscopic needles, which melt with decomposition at 207—209°. The second tetrahydroxyanthraquinone is extracted by means of dilute alcohol from the residue undissolved by benzene. It crystallises in small, red needles which do not melt at 380°; it sublimes in small, yellow needles, but is mostly decomposed. It dissolves readily in

alcohol, glacial acetic acid, and acetone, sparingly in ether and water. The solution in sulphuric acid is brownish-yellow; that in caustic alkali emerald-coloured. The *tetracetyl-compound* crystallises in lemon-coloured prisms, which are very readily soluble in glacial acetic acid, alcohol, and chloroform; it melts at 189°. N. H. M.

Methylanthragallols. By E. L. Cahn (*Ber.*, **19**, 2333—2336; compare Abstr., 1886, 556).—1-*Methylanthragallol*,

$$C_6H_3Me<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)_3,$$

is prepared by heating orthotoluic acid (3 parts) with gallic acid (2 parts) for 12 to 15 hours up to 130—135°. It crystallises from alcohol in gold-coloured flakes consisting of microscopic needles. It sublimes in long, orange-coloured needles, and melts at 297—298° with decomposition. It is readily soluble in hot alcohol and glacial acetic acid, sparingly in benzene; it also dissolves in hot water, yielding a red solution. The *triacetyl-derivative* crystallises in sulphur-coloured microscopic plates melting at 208—210°, readily soluble in chloroform, acetone, hot alcohol, &c. When methylanthragallol is distilled with zinc-dust, a hydrocarbon, crystallising in white plates and melting at 197°, is formed. When oxidised, it is converted into a quinone melting at 278—279°.

3-*Methylanthragallol* is prepared in a manner similar to the above compound from paratoluylic acid. It melts at 275°, and sublimes in orange-coloured needles. It resembles its isomeride. The *triacetyl-derivative* crystallises in well-formed, lustrous, golden prisms melting at 203—208° with decomposition.

2-*Methyl-* and 4-*methyl-anthragallol* are formed simultaneously from metatoluylic and gallic acids. The separation of the isomerides is difficult, and is best performed by converting the mixed product into the acetyl-derivative and recrystallising repeatedly from glacial acetic acid. The one methylanthragallol has a slight golden lustre, and melts at 312—313°; the other crystallises in small, well-formed prisms melting at 235—240°. The *acetyl-derivatives* melt at 188—190° and at 217—218° respectively.

The four methylanthragallols closely resemble one another and anthragallol. They are readily soluble in alcohol, and dissolve in strong and in dilute alkalis, yielding green and violet solutions respectively. The solution in hot ammonia has a fine blue colour, in sulphuric acid it is red; the latter changes to green on addition of a trace of nitric acid. The absorption-spectra of the red solutions of anthragallol and of the methylanthragallols in sulphuric acid are almost the same. N. H. M.

Acid from Santonin: Isophotosantonic Acid. By S. Cannizzaro and G. Fabris (*Ber.*, **19**, 2260—2265).—*Isophotosantonic acid*, $C_{15}H_{22}O_5$, is obtained by exposing 1 kilo. of santonin dissolved in 52 litres of acetic acid to the action of light for several months; one-ninth of the acetic acid is then boiled off under diminished pressure, and the

residue filtered from the photosantonic acid which separates on cooling. A further quantity of photosantonic acid is precipitated by adding water. The solution is then nearly free from photosantonic acid and still contains almost the whole of the isomeride. It is treated with sodium carbonate (which dissolves the photosantonic acid alone) and extracted with ether. It separates from its alcoholic solution in thick, triclinic crystals, rather soluble in ether, and sparingly in water. When heated at 100°, it is converted into the lactone, $C_{15}H_{20}O_4$. It is dextrorotatory, $[\alpha]_D = +124° 17'$. Photosantonic acid has nearly the same specific rotatory power, but is lævorotatory. Isophotosantonic acid dissolves in alkalis and in warm solutions of alkaline carbonates; the solutions are orange-red. The *barium salt*, $(C_{15}H_{21}O_5)_2Ba + H_2O$, is an amorphous powder, readily soluble in alcohol and in water. The *monacetyl-compound* crystallises from alcohol in transparent needles which melt at 183°; it is dextrorotatory, $[\alpha]_D = +58° 16'$. The *diacetyl-compound* is very sparingly soluble; it melts at 163—166°. It is very unstable, and when often recrystallised changes to the monacetyl-derivative.

The results above described point to the following constitutional formulæ for the lactones of isophotosantonic and photosantonic acids respectively:—

$$\begin{array}{l} CH:CH\cdot CH\cdot CHMe\cdot C(OH)_2 \\ | \quad\quad | \quad\quad | \\ CH:CH\cdot CH\cdot CHMe\cdot CH\cdot CH<\begin{matrix}CH_2\\O\text{—}\end{matrix}>CO \end{array} \text{ and}$$

$$\begin{array}{l} CH:CH\cdot CH\cdot CHMe\cdot COOH \\ | \quad\quad | \\ CH:CH\cdot CH\cdot CHMe\cdot CH_2\cdot CH<\begin{matrix}CH_2\\O\text{—}\end{matrix}>CO. \end{array}$$

N. H. M.

Cinchol. By O. Hesse (*Annalen*, **234**, 375—379).—A further comparison of the properties of cinchol and Liebermann's oxyquinoterpene or cholestole (Abstr., 1885, 1075) confirms the author's previously expressed opinion (Abstr., 1885, 1076) that these two substances are identical. They both melt at 115°, and are identical in crystalline form. The acetates melt at 124°, and also exhibit identical crystalline forms. W. C. W.

Alkaloïds. By O. de Coninck (*Compt. rend.*, **103**, 640—641.)—Piperidine methiodide gives no colour reaction with potassium hydroxide (Abstr., 1886, 897), and this difference furnishes a means of distinguishing between a pyridic base and its hexhydride.

Cicutine methiodide also gives no colour reaction, but the solution acquires an amber tint. The reaction is always obtained with collidines, and therefore will most probably be given by conyrine, the collidine of which cicutine is the hexhydride.

No similar colour reaction is obtained with the methiodides of aniline, orthotoluidine, or metaxylidine. When methiodides of pyridic bases are mixed with a fragment of solid potassium hydroxide

and sufficient water to form a paste, and then heated, a peculiar odour is developed owing to the formation of pyridic dihydrides.

No similar reaction is given by methiodides of pyridic hexhydrides, nor by the methiodides of aniline and its homologues. C. H. B.

Extraction of Pyrroline from Animal Oil. By G. L. Ciamician and M. Dennstedt (*Gazzetta*, **16**, 336).—Pyrroline may be extracted as the potassium-derivative by using caustic potash instead of the metal as heretofore practised. The reaction is probably $C_4H_4NH + KOH = C_4H_4NK + H_2O$; the excess of potash serving as a dehydrating agent. The fraction of the oil, freed previously from nitriles, which passes over at 125—140°, is heated in an oil-bath with an excess of fused potash, using a reflux apparatus. At the conclusion of the reaction, the liquid separates into three layers, the heaviest of which is the excess of potash, the next the potassium compound, and the lightest the unaltered hydrocarbons. On cooling, the potassium compound solidifies, and is washed with anhydrous ether. The substance thus obtained, distilled in a current of steam, yields pyrroline of boiling point 130—138°; with chloroform, it yields chloropyridine (Abstr., 1881, 820). V. H. V.

Pyridine Bases. By A. Ladenburg (*Compt. rend.*, **103**, 692—695; see also Abstr., 1884 and 1885).—*α-Methylpyridine* (picoline), C_6NH_7, is obtained in the form of hydriodide by heating pyridine methiodide at 300°. The base boils at 128—129°, and is miscible with alcohol and water; sp. gr. at 0° = 0·9656. It forms a characteristic mercuriochloride, $C_6NH_7,HCl,HgCl_2$, by means of which it can be isolated in a state of purity; this compound is very soluble in hot water, but only slightly soluble in cold water. *β-Methylpyridine* is best prepared by Zanoni's method of heating glycerol and acetamide with phosphoric anhydride. It boils at 142°; sp. gr. at 0° = 0·9771. The platinochloride crystallises with 1 mol. H_2O and melts at 214°; the aurochloride is anhydrous and melts at 183°; the mercuriochloride is also anhydrous, melts at 143°, and forms slender needles which can be crystallised from water. *γ-Methylpyridine* is formed only in small quantity by the action of heat on pyridine methiodide; it boils at 144—145°; sp. gr. at 0° = 0·9708. The platinochloride is anhydrous, melts at 225°, and is only slightly soluble in water. *αα'-Dimethylpyridine* is isolated from the fraction of animal oil boiling at 138—145° by means of the mercuriochloride, $C_7NH_9,HCl,HgCl_2$, which can be crystallised from water, and melts at 183°. When decomposed, it yields lutidine boiling at 142—143°; sp. gr. at 0° = 0·9424. The aurochloride forms yellow needles which melt at 124°; the platinochloride crystallises in large monoclinic crystals isomorphous with β-picoline platinochloride, although the former is anhydrous, whilst the latter contains 1 mol. H_2O. The picrate is only slightly soluble in water and melts at 159°. When the base is oxidised, it yields a bibasic acid, $C_5NH_3(COOH)_2$, crystallising in beautiful needles which melt at 226°, and at the same time decompose into pyridine and carbonic anhydride. *α-γ-Dimethylpyridine* exists in large quantity in Dippel's

oil, and can be isolated from the fraction which boils at 155—160° by acidifying with hydrochloric acid and adding mercuric chloride. The precipitated mercuriochloride, $2(C_7NH_9,HCl,2HgCl_2) + H_2O$, is repeatedly recrystallised, and forms beautiful needles which melt at 129°. When decomposed, it yields the base; this boils at 157°, and is only slightly soluble in cold water, still less soluble in hot water. The platinochloride is somewhat soluble, crystallises readily, and melts at 219—220°. The aurochloride, $C_7H_9N,HAuCl_4$, is less soluble and does not crystallise so well. The picrate melts at 180°. This lutidine is identical with the lutidine prepared synthetically by Hantzsch. When oxidised, it yields lutidinic acid, which crystallises in plates which melt at 235°.

α-Ethylpyridine is the principal product of the action of a high temperature on pyridine ethiodide; it boils at 150°, is miscible with alcohol, but is only slightly soluble in water. The platinochloride is somewhat soluble in water, and melts at 168—170°; the aurochloride melts at 120° and crystallises readily from hot water; the picrate melts at 110°. When the base is oxidised, it yields picolinic acid only. *γ-Ethylpyridine* is also formed in smaller quantity by the action of heat on pyridine ethiodide, and is separated from its isomeride by taking advantage of the comparative insolubility of its salts, especially the platinochloride or ferrocyanide. The base boils at 165°; sp. gr. at 0° = 0·9522. The platinochloride melts at 208°, the picrate at 163°, the aurochloride at 138°. The ferrocyanide is precipitated even from very dilute solutions. When the base is oxidised, it yields isonicotinic acid. *α-γ-Diethylpyridine* is also obtained in small quantity by the action of heat on pyridine ethiodide; it boils at 187—188°, has a disagreeable odour, and is only slightly soluble in water. When carefully oxidised, it yields lutidinic acid which melts at 235°.

α-Isopropylpyridine, obtained by heating pyridine with propyl or isopropyl iodide at 300°, boils at 158—159°, is slightly soluble in water, and has a very disagreeable odour; sp. gr. at 0° = 0·9342. The platinochloride, $(C_8H_{11}N)_2,H_2PtCl_6$, is somewhat soluble and melts at 168°; the aurochloride crystallises from dilute solutions in yellow plates which melt at 91° and are only slightly soluble in water; the picrate forms yellow needles which melt at 116°. When the base is oxidised by potassium permanganate, it yields picolinic acid. *γ-Isopropylpyridine* is obtained in smaller quantity by the same reaction, and is separated by means of the platinochloride, which is only slightly soluble in water, and melts at 203°. The base boils at 177—178°; sp. gr. at 0° = 0·9439. When oxidised, it yields isonicotinic acid.

C. H. B.

Quinoline. By A. Claus and F. Collischonn (*Ber.*, **19**, 2502—2508).—The authors describe a number of halogen additive products of the propio-haloïd compounds of quinoline. Quinoline propiobromide is easily formed when its constituents are heated alone, or better, with alcohol, at 90—100°. It is easily soluble in alcohol and water, and crystallises from water in colourless plates containing 2 mols. H_2O, and melting at 66°; from absolute alcohol, it separates in anhydrous crystals melting at 148°. It is easily soluble in chloroform, and from this solution crystallises with 1 mol. $CHCl_3$ in quadratic

prisms which gradually lose chloroform and become opaque, soften at 65°, and melt with evolution of chloroform at 128—129°. *Quinoline propiodide* forms yellow anhydrous crystals melting at 145°, and becoming rapidly discoloured in the light. This also crystallises with 1 mol. $CHCl_3$ in quadratic prisms which begin to evolve chloroform at 92°. *Quinoline propiochloride* cannot be easily prepared directly from its constituents, but is best obtained by acting on the corresponding bromide with silver chloride. It is very soluble in water, and crystallises in colourless prisms or plates containing 1 mol. H_2O and melting at 95°. The hygroscopic anhydrous salt melts at 135°; it also crystallises with 1 mol. $CHCl_3$ in quadratic prisms melting at 79°.

The additive products were obtained by treating a chloroform solution of the propiohaloïd salt with the halogen.

Quinoline propiobromide dibromide, $C_9NH_7{\cdot}PrBr_2$, forms glistening, red, triclinic crystals melting at 93°. The *di-iodide* forms brown metallic needles melting at 60°. The *dichloride* forms yellow scales melting at 60°. The *tetriodide*, $C_9H_7N{\cdot}PrBrI_4$, yields small, almost black needles having a green fluorescence and melting at 49°.

Quinoline propiodide dibromide forms orange triclinic crystals melting at 77°. The *di-iodide* forms thin, bronze-coloured scales melting at 62°. The *dichloride* forms yellow needles melting at 87°. The *tetrabromide*, $C_9NH_7{\cdot}PrIBr_4$, is a very unstable orange-red powder which evolves bromine at the ordinary temperature, and gave no constant melting point (48—58°). The *tetriodide* forms iodine-coloured plates melting at 50°. The *tetrachloride* crystallises in needles which show the high melting point 144—145°. It is also formed when quinoline propiochloride is treated with iodine trichloride, and may therefore really be quinoline propiochloride iodide trichloride. When boiled with water, it is gradually decomposed into quinoline propiochloride. Similar migration of the halogen-atoms may also very likely take place in others of the mixed haloïd compounds.

Quinoline propiochloride dibromide forms orange crystals melting at 84—85°. The *di-iodide* melts at 61—62°. The *dichloride* is very unstable and could not be obtained in a pure state. A tetriodide is easily formed, but could not be obtained in a pure state.

All these additive compounds decompose when heated at 150—200°, propyl haloïd salts, quinoline haloïd salts, and halogenised and alkylated quinolines being amongst the products of decomposition. These decompositions are being studied. All the above temperatures are uncorrected. L. T. T.

Isoquinoline and its Derivatives. By S. Gabriel (*Ber.*, 19, 2354—2363; compare Abstr., 1886, 812).—*Dichlorisoquinoline*,

$$C_6H_4<\begin{matrix}CH:CCl\\CCl:N-\end{matrix}>,$$

is prepared by heating homo-orthophthalimide (8 grams) with phosphorus oxychloride (24 grams) for three hours at 150—170°. The product is poured into alcohol (5 vols.), the mass of crystals so obtained treated with soda until alkaline, filtered, and recrystallised from alcohol. It is readily soluble in hot alcohol, cold chloroform,

ether, and benzene; it boils at 305—307°. The alkaline mother-liquor obtained in the preparation of this compound, when treated with hydrochloric acid, yielded the *chloro-derivative* $C_6H_4<^{CH_2\cdot CO}_{CCl:N}>$, or $C_6H_4<^{CH:C(OH)}_{CCl:N}>$; this crystallises from boiling alcohol in long needles melting at 195—197° with evolution of gas. It is rather soluble in hot alcohol, sparingly in hot benzene and in chloroform; it dissolves in alcohol, but not in ammonia. The *methyl-compound*, $C_9H_5MeClNO$, is obtained by dissolving half a gram of the substance in methyl alcohol (10 c.c.), adding methyl iodide (2 grams), and heating at 100°. It forms slender, white crystals, readily soluble in alcohol, ether, benzene, &c., insoluble in alkali. It melts at 66—67°, and has an odour of fruit.

Chlorisoquinoline, $C_6H_4<^{CH:CCl}_{CH:N-}>$, is obtained by reducing the dichloro-compound with phosphorus and hydriodic acid at 150—170°, or with tin and hydrochloric acid. It melts at 47—48°, and boils at 280—281° under 753 mm. pressure, and is readily soluble.

Methoxyphenylchlorisoquinoline, $C_6H_4<^{CCl:CPh-}_{C(OMe):N}>$, is formed when phenyldichlorisoquinoline (1 gram) and sodium methoxide are heated for three hours at 100°. It crystallises from alcohol in needles melting at 76°, readily soluble in ether, benzene, &c. It dissolves also in strong hydrochloric acid, but is precipitated by water. When heated with fuming hydrochloric acid at 100°, it is converted, with evolution of methyl chloride, into the compound $C_{15}H_{10}ClNO$, probably *chlorisobenzal phthalimidine*, $C_6H_4<^{CCl:CPh}_{CO\cdot NH-}>$. It crystallises from alcohol in slender, lustrous needles, melting at 211—212°, moderately soluble in ether and cold alcohol, readily in glacial acetic acid, benzene, &c. The formation of this compound is analogous to that of isobenzalphthalimidine from phenylethoxyisoquinoline (Abstr., 1886, 631).

Ethoxychlorisoquinoline, $C_6H_4<^{CH=CCl-}_{C(OEt):N}>$, is prepared by heating dichloroisoquinoline with alcoholic soda at 100°. It forms readily soluble needles melting at 37—37·5°.

The *methoxy-derivative*, $C_{10}H_8NOCl$, is prepared in a similar manner. It melts at 73—74°, and is isomeric with the methyl-compound obtained from chloroxyquinoline. When heated at 150° in a current of dry hydrogen chloride, it is converted into *oxychlorisoquinoline*, $C_6H_4<^{CH:CCl}_{CO\cdot NH-}>$. This crystallises from dilute alcohol in slender needles melting at 218—220°; it dissolves rather readily in ether, easily in alcohol and chloroform; it is also readily soluble in dilute aqueous soda. The *methyl-derivative*, $C_6H_4<^{CH:CCl}_{CO\cdot NMe}>$, crystallises in long, broad needles which melt at 111—112°; it is readily soluble. Oxychlorisoquinoline is formed in small quantities in the preparation of ethoxychlorisoquinoline.

Isoquinoline is conveniently prepared by heating dichlorisoquinoline (3 grams), and hydriodic acid, sp. gr. 1·96 (18 c.c.) for five hours at 230°. The product is treated with alkali, and steam distilled; the distillate being treated with hydrochloric acid and again steam distilled to remove the unchanged chloro-base. Isoquinoline melts at 20—22°, and boils at 236—236·5°. The *ethiodide* crystallises in gold-coloured plates melting at 147—148°, readily soluble in water and in warm alcohol. N. H. M.

Synthesis of Hydroxyquinolinecarboxylic Acid. By E. Lippmann and F. Fleissner (*Ber.*, **19**, 2467—2471).—Unlike ordinary phenol-derivatives, the potassium compound of orthohydroxyquinoline is not acted on by carbonic anhydride even at 300°. When, however, nascent carbonic anhydride (obtained by the action of potash on carbon tetrachloride) is employed, action takes place. Orthohydroxyquinoline, carbon tetrachloride, and caustic potash are mixed in alcoholic solution in the proportions necessary for the equation $C_9NH_7O + CCl_4 + 6KHO = 4KCl + C_9NH_5(OK)\cdot COOK + 4H_2O$, and the whole boiled for 12 hours. The product contains *hydroxyquinolinecarboxylic acid*, $OH\cdot C_9NH_5\cdot COOH$, which when purified crystallises in yellow prisms melting at 280°. This acid agrees in its salts and in all its properties, save melting point and oxidation products, with the α-hydroxycinchonic acid (m. p. 254—256°) obtained by Weidel and Cobenzl from sulphocinchonic acid (Abstr., 1881, 742). The acid is sparingly soluble in the ordinary solvents. It dissolves in dilute hydrochloric acid to form a *hydrochloride*, which is precipitated on the addition of concentrated hydrochloric acid in the form of glistening needles. The *platinochloride* forms unstable, bright yellow needles. The acid forms a *normal barium* salt, the pale yellow solution of which, on the addition of baryta-water, yields white needles of the *basic barium* salt $C_{10}NH_5BaO_3 + H_2O$; these only part with their water of crystallisation at 140—150°. The *silver* salt is precipitated in the form of pale lemon-yellow flocks, which soon change to microscopic needles. The aqueous solution of the acid gives a green coloration with ferric chloride, but none with ferrous sulphate. When subjected to dry distillation, the acid yields orthohydroxyquinoline.

When oxidised by potassium permanganate in alkaline solution, the acid yields a *pyridinedicarboxylic acid*, $C_7NH_5O_4$, forming bright yellow crystals melting at 234—235°. With ferrous sulphate, it gives a blood-red coloration, and forms a silver salt which is gelatinous when first precipitated, but soon becomes crystalline. This acid is probably identical with Böttinger's pyridinedicarboxylic acid, and isomeric with Weidel's isocinchomeronic acid.

Weidel and Cobenzl's α-hydroxycinchonic acid, when similarly oxidised, yields α-pyridinetricarboxylic acid. The authors are further investigating this subject. L. T. T.

Peculiar Formation of β-Diquinoline. By O. Fischer and H. van Loo (*Ber.*, **19**, 2471—2476).—This is a continuation of the authors' previous work (Abstr., 1884, 1372). When β-diquinoline is heated with ethyl iodide in closed tubes at 90—100°, *β-diquinoline*

ethiodide, $C_{18}N_2H_{12}EtI$, is formed in long, ruby-red crystals. It is very unstable, and is decomposed by water and by boiling alcohol. No diethiodide could be obtained. When bromine is allowed to act on β-diquinoline in chloroform solution, a *tetrabromo-additive product*, $C_{18}N_2H_{12}Br_4$, is produced. This crystallises in pale yellow needles melting at 192°, and is decomposed at once by sulphurous acid, diquinoline sulphate being formed. *β-Diquinolinedisulphonic acid*, $C_{18}N_2H_{10}(SO_3H)_2$, is produced when β-diquinoline is heated with a large excess of fuming sulphuric acid. It is very soluble in water, and is precipitated from this solution by a mixture of alcohol and ether in yellowish flocks. Its *potassium salt* crystallises from 50 per cent. alcohol in glistening white prisms containing 3 mols. H_2O. The anaquinolinecarboxylic acid described in the former paper (*loc. cit.*), as obtained by the oxidation of the base by chromic acid in acetic solution, is undoubtedly identical with that lately obtained by Skraup and Brunner (m. p. 247°). The melting point previously given by the authors was obtained from a sample crystallised from benzene; when crystallised from water, it melts at 248—249°. The author considers this acid to be metaquinolinecarboxylic acid, and that the name anaquinolinecarboxylic acid should be transferred to the acid melting at 357°, and hitherto designated metaquinolinecarboxylic acid.

If chromic acid is dissolved in sulphuric acid in place of acetic acid, the oxidation takes place in quite a different way. Under these circumstances *pyridylquinolinecarboxylic acid*, $C_9NH_6{\cdot}C_5NH_3{\cdot}COOH$, is formed. This crystallises in glistening needles, which melt with decomposition at 271—273°. It is sparingly soluble in water, easily in alcohol, and forms salts both with acids and bases. The silver salt, when heated, yields a *pyridylquinoline*, $C_{14}N_2H_{10}$, which crystallises in white needles melting at 104°, and gives a reddish-yellow crystalline *platinochloride*. L. T. T.

Piperidine Bases. By A. Ladenburg (*Compt. rend.*, **103**, 747—749).—The bases are obtained by treating boiling alcoholic solutions of the corresponding pyridine bases with a large excess of sodium.

Piperidine obtained in this way is identical with the base prepared from piperine. *α-Methylpiperidine* or *α-pipecoline* boils at 118—119°, has the same odour as piperidine, and dissolves readily in water; sp. gr. at 0° = 0·860. The hydrochloride is very soluble, but not deliquescent, and melts at 189°. The hydrobromide is less soluble, and forms confused needles which melt at 182°; the platinochloride is very soluble. With carbon bisulphide, the base yields a thiocarbamate, $CS_2{,}2C_6H_{13}N$, which crystallises readily, melts at 118°, and is analogous to that formed from piperidine. *β-Methylpiperidine* or *β-pipecoline* boils at 125°, and dissolves readily in water; sp. gr. at 0° = 0·8684. The hydriodide crystallises in beautiful, non-deliquescent needles, which melt at 131°. It combines with cadmium iodide, forming the compound $CdI_2{,}2C_6H_{13}NHI$, a white precipitate soluble in warm water, from which it crystallises in white tables melting at 145°. The platinochloride is somewhat soluble, and forms orange prisms melting at 192°; the aurochloride is very soluble, and melts at 131°; the picrate melts at 136°. *αα′-Dimethylpiperidine* or *αα′-lupetidine* boils at 128—

130°, and is very soluble in water and alcohol; sp. gr. at 0° = 0·8492. The hydrochloride and hydrobromide crystallise in non-deliquescent needles; the platinochloride forms large orange crystals which melt at 212°. *αγ-Dimethypiperidine* boils at 141°, has an odour of piperidine, and dissolves readily in water, though not in all proportions; sp. gr. at 0° = 0·8615. The hydrochloride crystallises in beautiful needles which melt at 235°; the hydrobromide is even more soluble; the platinochloride is not very soluble, and crystallises in nodules; the aurochloride is an oil. *α-Ethylpiperidine* boils at 143°, and dissolves slightly in water, but separates from the solution on heating, and has an odour resembling that of piperidine and conicine; sp. gr. at 0° = 0·8674. The hydrochloride forms non-deliquescent crystals; the platinochloride crystallises in large tables which melt at 178°. The methyl-derivative boils at 149—152°; sp. gr. at 0° = 0·8495. *γ-Ethylpiperidine* boils at 157°, has a disagreeable odour, is only slightly soluble in cold water, and still less soluble in warm water; sp. gr. at 0° = 0·8795. The hydrochloride is deliquescent; the platinochloride forms yellow tables which melt at 170—173°; the aurochloride crystallises from warm water in lamellæ which melt at 105°. *α-Isopropylpiperidine* boils at 160—162°, and is slightly soluble in water, but separates from the solution when gently heated; sp. gr. at 0° = 0·8676. Its odour and its properties generally resemble those of its isomeride, conicine, but it is much less poisonous. The platinochloride is much less soluble in water, and is not soluble in alcohol or ether; it melts at 193°; the hydrochloride melts at 240°, the hydrobromide at 230°, the hydriodide at 242°. All these derivatives crystallise readily. The iodide combines with cadmium iodide, forming a slightly soluble double salt, which crystallises readily and melts at 132°. The picrate and aurochloride crystallise readily, and are only slightly soluble. With carbon bisulphide, the base yields a crystalline compound, $CS(C_8H_{16}N)SH,C_8H_{17}N$, which melts at 105°, dissolves readily in alcohol, but is only slightly soluble in water. The methyl-derivative of α-isopropylpiperidine boils at 166°; sp. gr. at 0° = 0 8593. Its hydrochloride is extremely soluble in water; the aurochloride forms shining lamellæ, and is also very soluble in water; the platinochloride is somewhat soluble, and melts at 100°; the picrate crystallises readily, and melts at 149°. *γ-Isopropylpiperidine* boils at 168—171°, dissolves slightly in water, and has a very disagreeable odour. The hydrochloride crystallises, but is not stable in moist air; the platinochloride is crystalline, and is only slightly soluble in water, but dissolves in alcohol and ether, and melts at 172°; the aurochloride is also crystalline, and only slightly soluble. C. H. B.

Method of Preparing Extracts of Pepsin. By W. Podwyssozki (*Pflüger's Archiv*, **39**, 62—74).—If the gastric mucous membrane of carnivora and herbivora be placed in glycerol almost immediately after death, very little pepsin is extracted.

Ebstein and Grützner state that glycerol dissolves pepsin only, but the author finds that a certain amount of pepsin precursor, or as he terms it "propepsin," is dissolved also.

Mucous membrane exhausted with glycerol still yields an important

amount of pepsin when treated with hydrochloric acid or hydrochloric acid and glycerol. It appears, therefore, that gastric mucous membrane contains two propepsins, one soluble in glycerol, the other insoluble.

If the mucous membrane is kept in a warm place for 24 hours before it is extracted, a much larger yield of pepsin is obtained, provided no putrefaction has set in.

Hydrogen and carbonic anhydride have no influence on the formation of pepsin, but oxygen, on the other hand, appears to favour its development; more pepsin is formed when the mucous membrane is allowed to remain in contact with oxygen than when it is in contact with air.

Chlorine gas passed through any extract entirely destroys the ferment. J. P. L.

Comparative Estimation of Preparations of Pepsin. By A. A. Lipski (*Russkaya Meditsina*, **35**, 583—584).—The powdered pepsins were examined by digesting 0·2 gram of the preparation with 10 grams of white of egg and 100 c.c. of hydrochloric acid (0·25 per cent.) for four hours at 40°. The undissolved albumin being then determined, the weight of this in grams was:—Perret acidifié 8·756, Marquart 8·577, Lamatch 8·557, Merck 7·213, Boudault neutre (No. 4) 2·62, Witte 2·195, Boudault acidifié 1·2, Russicum solubile (of the Russian Ph.) 0·721, do. do. recent 0·47, do. do. without the sugar contained in the official preparation 0·157. The Russian pepsin is, therefore, far more active than any of the German or French preparations tested. The same holds good for the pepsin wines.

T. M.

Physiological Chemistry.

Sugar in the Blood with Reference to Nutrition. By J. Seegen (*Pflüger's Archiv*, **39**, 121—131).—Experiments on dogs have shown (Abstr., 1886, 382 and 411) that the percentage of sugar is always approximately twice as great in the blood of the hepatic as in the blood of the portal vein during various carbohydrate diets and during long periods of inanition, also that peptone is probably the chief constituent from which the liver forms sugar under normal conditions. The sugar formed in one day during starvation is far in excess of the total glycogen present in the body.

Further experiments have been made on dogs fed with a diet of meat only, of fat with a minimal quantity of meat, and in some instances with fat only.

The general result is the same as in previous experiments, namely, that the percentage of sugar in the blood leaving the liver is double that of the blood on entering. The total amount of sugar in the blood as well as the difference between the percentages in the blood

on entering and leaving the liver is greater with a meat diet than any other.

The most striking result is the continued formation of sugar during an almost exclusively fat diet. It might be supposed that this is due to proteïd decomposition, but a determination of the nitrogen excreted during the feeding was quite insufficient to account for the increase.

The amount of blood passing through the liver of dogs of 10 to 12 kilos. is not less than 200 litres in the 24 hours. The mean difference in the percentage of sugar of the blood on entering and leaving the liver is 0·1 per cent., consequently about 200 grams of sugar would be formed in 24 hours. During the fat diet, the amount of nitrogen excreted daily was on an average 15 grams, corresponding to 100 grams of proteïd, a quantity quite insufficient to furnish 200 grams of sugar, even supposing that none of the carbon of the proteïd be utilised for the formation of urea.

The conclusion drawn from these experiments is that the liver has the power of forming sugar from fat. This would satisfactorily explain the constant formation of sugar during starvation, for Voit has shown that an animal during starvation loses 97 per cent. of its fat, and only 30 per cent. of its muscular substance.

The chief results of the author's experiments may be thus summed up:—

1st. The blood of the hepatic vein is without exception richer in sugar than the blood of the portal vein.

2nd. The new formed sugar does not depend on the sugar and carbohydrates ingested with the food.

3rd. The glycogen of the liver is not concerned in the formation of sugar.

4th. Albumin and fat are the materials from which the liver forms sugar. J. P. L.

Power of the Liver to Form Sugar from Fat. By J. Seegen (*Pflüger's Archiv*, **39**, 132—142).—It has been previously shown that small pieces of freshly excised liver in the presence of defibrinated blood have the power of converting peptone into sugar (Abstr., 1886, 382). By a similar series of experiments, the author has proved that the liver cells can under the same conditions convert fat into sugar, thus confirming the conclusion he arrived at from his experiments on feeding dogs on a diet consisting exclusively of fat (preceding Abstract).

For each experiment, 50 grams of finely cut liver excised from a recently killed dog was mixed with 60 to 80 c.c. of freshly defibrinated blood and placed in a large flask; to this mixture various emulsions of vegetable oils were added. The flask and contents were maintained for 5 or 6 hours at 35° to 40°, and a constant stream of air was drawn through the mixture of blood by means of an aspirator.

The average increase in the percentage of sugar was found to be 50 per cent. Control experiments were made in every instance.

A further series of experiments proved that both constituents of a fat, that is both glycerol and the fatty acid, are alike capable of being converted into sugar by the liver. J. P. L.

Importance of Ammonia for the Formation of Glycogen in the Liver of the Rabbit. By F. Röhmann (*Pflüger's Archiv*, **39**, 21—53).—Asparagine and glycocine given with a carbohydrate diet increase the amount of glycogen formed in the liver to a marked extent; this increase is more pronounced with asparagine than with glycocine. On account of its slight solubility, asparagine is probably not absorbed unchanged, but undergoes decomposition with formation of ammonia.

Ammonium carbonate given with the same diet increases the glycogen in a still more marked manner, but ammonia in the form of lactate seems to be inert.

As sodium carbonate and hydrogen carbonate have no effect, ammonium carbonate does not exert its influence by reason of its alkalinity.

As a possible explanation, the author suggests that the ammonia and a carbohydrate entering the liver cells together may form a new compound which will split into glycogen on the one hand and a nitrogenised product on the other, for instance, urea. J. P. L.

Feeding and Development of Silkworms. By O. Kellner (*Landw. Versuchs-Stat.*, 1886, 381—392).—This article contains an account of experiments which are a continuation of those previously detailed (Abstr., 1884, 1202). The research was commenced with the view of determining what quantity of food was necessary for the full and healthy development of the worm, with the largest subsequent supply of silk. Without entering into the details of feeding, &c., all of which are fully given in tables, it will be sufficient to give the final results. Every increase of growth requires an increase in the food, but this increase in food is not commensurate with the growth, being very much higher; the weaker the insect is before envelopment, the greater will be the loss during metamorphosis, by respiration, &c.

A poorly fed and developed caterpillar produces a lower yield of valuable silk than those which are well and largely fed, and will contain more nitrogenous and mineral matter, whilst the well-fed insect will be richer in fat and other non-nitrogenous matter. E. W. P.

Isethionic Acid in the Body, and Thiosulphuric Acid in the Urine. By E. Salkowski (*Pflüger's Archiv*, **39**, 209—222).—In a former paper (*Virchow's Archiv*, **66**, 315), the author stated that in the dog the administration of sodium isethionate produced an increase of sulphuric acid in the urine, but that thiosulphuric acid was under all circumstances absent. Heffter (*Pflüger's Archiv*, **38**, 476) states however, that sulphuric acid is not formed from isethionic acid, but that the greater part (78 per cent.) of the latter acid leaves the body as thiosulphuric acid, and a smaller portion (22 per cent.) in some undiscovered manner. Heffter himself explains the discrepancy by supposing it to be due to the difference in diet during the investigation, Heffter using meat, not bread and milk as in Salkowski's earlier experiments.

The present research is a reinvestigation of the subject: a dog was

fed on a fixed meat diet, and for three days 3 grams of sodium isethonate was given *per diem*. The results are shown in the following table:—

Day.	Diet.	Nitrogen in urine.	Sulphuric acid in urine.
1	Meat	12·22	3·20
2	Do.	12·49	3·15
3	Do.	12·49	2·97
4	3 gr. of drug added	12·49	3·83
5	Do.	12·23	4·65
6	Do.	12·25	4·99
7	Meat	12·04	3·40
8	Do.	11·63	2·89
9	Do.	11·49	3·16

This table shows that whereas the nitrogen output remains constant, the amount of sulphates is increased; the increase could therefore not have been due to increased metabolism of proteïds; it is therefore all due to the isethionic acid, and it is found from the foregoing numbers, that 30 per cent. of the isethionic acid must have become oxidised into sulphuric acid. By comparing the intensity of the sulphuretted hydrogen reaction, it was found also that the amount of thiosulphuric acid in the urine was slightly increased. The amount of this acid in the urine was estimated also by its reducing action on potassium permanganate; the increase during the days when the drug was given, show theoretically that 13·4 per cent. of the sulphur of the isethionic acid pass out of the body in the form of thiosulphuric acid, a figure which is shown by control experiments to be too high, as the urine contains other easily oxidisable substances. The question as to what becomes of the remainder of the sulphur is not entered into. There seems also to be no way of reconciling the present results with those obtained by Heffter.

The aromatic sulphonic acids pass out unchanged in the urine, no thiosulphates being formed; this also is contradictory to the statements of Heffter. W. D. H.

Trypsin in Urine. By H. Leo (*Pflüger's Archiv*, **39**, 246—264).—Since the publication of the author's paper (Abstr., 1886, 381) in which he showed that trypsin did not exist in the urine, Gehrig (*Pflüger's Archiv*, **38**, 35) states he has found trypsin in the urine; pieces of fibrin stained with magdala-red, soaked in urine, and transferred to 1 per cent. soda solution undergo digestion in a few hours; this cannot be due to putrefaction as it is so rapid; it is however prevented by the admixture of thymol with the digesting mixture; this is explained by saying that thymol hinders pancreatic digestion. The present research is a reinvestigation of the subject, the urine of healthy men and dogs being employed. It is found that thymol does not hinder pancreatic digestion. A very weak solution of the tryptic ferment was prepared by adding a drop of glycerol extract of pancreas to a litre of water. This excited no digestive action on fibrin. After pieces of fibrin had been soaked in it for

24 hours, however, and then transferred to a 1 per cent. soda solution they underwent digestion, as they had absorbed the ferment. With the urine, however, no such result ever occurred; that is, urine, if it contains trypsin at all, contains a less amount than the weak solution of it obtained by adding a drop of extract of pancreas to a litre of water. W. D. H

Chemistry of Vegetable Physiology and Agriculture.

The Bacillus of Panary Fermentation. By E. Laurent (*Bied. Centr.*, 1886, 648).—The author says that the surface of wheat, rye, and other food grains contains spores of bacilli which in grinding pass into the flour, and when made into dough they germinate, evolve carbonic anhydride, and raise the bread. When cultivated on gelatin, it develops characteristic cultures different from other bacilli, and has been given the name of *Bacillus panificans;* it exists with or without oxygen, and renders albumin and gluten soluble; it also grows in saccharose and in a weak solution of boiled starch; it withstands the heat of boiling water, if at a depth of 7 or 8 mm. in the bread; it is abundant in bread which has been eaten, and is found freely in the fæces. It can attack starch after baking, if the medium is not sufficiently acid, and causes a disease in bread which the author has often observed, and calls viscid or clammy bread; the addition of a sufficient quantity of an organic acid prevents this. J. F.

Decomposition of Silicic Acid by Leaves. By A. Denaro (*Gazzetta*, **16**, 328—330).—A few years ago Grimaldi stated in a pamphlet that silica is decomposed by leaves exposed to sunlight, precisely as carbonic anhydride is, into the element and oxygen. It is probable, however, that sufficient care was not taken to exclude carbonic anhydride derived from the potassium carbonate, as an impurity in the silica. Accordingly the author has repeated the experiments with a sample of silicic acid obtained from a sodium silicate produced by the direct fusion of sodium oxide with silica. Comparative experiments were made with leaves of which some were previously deprived of air, whilst others were introduced directly into the solution of silicic acid. In the former case, no oxygen was evolved, in the latter only a small quantity. Further, it is shown that no silica is absorbed by the leaves; the proportion of silica in them was found to be the same, whether or not they had been treated by the silicic acid solution. V. H. V.

Formation of Albuminoïds in Plants. By C. O. Müller (*Landw. Versuchs-Stat.*, 1886, 326—335).—From the experiments which have been made on many plants, it would appear that under normal conditions, plants contain asparagine, and this amide appears

if the growing parts are placed in darkness; but in fully grown portions, asparagine is only exceptionally found, and then only in traces.

If a portion of a plant is placed in darkness, by enveloping it in black paper, whereby it still remains connected with the parent, and the older portions are left undisturbed, then an accumulation of asparagine is formed, which when the light is admitted, is absorbed; This does not occur in the fully grown parts, save exceptionally. This result seems to show that the formation of asparagine is independent of carbohydrates, and also that the amide formed is not a bye-product of the interchange of matter within the plant. It has also been found that even when a plant is growing under abnormal conditions, when all carbonic anhydride has been removed from the air, asparagine is formed in the young parts, but not in the matured portions. Consequently it appears as if light played as inconspicuous a part in the formation of asparagine as carbohydrates. The author considers that asparagine is formed by the union of inorganic nitrogen compounds and malic acid within the plant, the acid being derived from the carbohydrates. E. W. P.

Observations on the Growth of Potatoes. By U. Kreusler (*Bied. Centr.*, 1886, 618—624).—The author has examined potatoes at different stages of their growth. At the time of sowing, large and small tubers were of the same specific gravity and composition; taken up shortly after the sowing, there was but little change observable, there was more moisture, due to partial exhaustion of their substance. Glucose was not found before planting, but was present in the germinating tubers; nitrogenous combinations diminished considerably in the growing roots.

The young tubers gradually developed dry matter, principally starch, in proportion as they grew. Glucose was present at the beginning, but gradually decreased as they ripened, when it disappeared. Substances which reduced copper were absent from the very young plants, but appeared at a later stage to disappear when fully ripe; the amount of carbohydrates in the sap was twice as much in the young as in the ripe tubers.

In the stalks and leaves, cellulose and non-nitrogenous extract increased, raw proteïn and fat decreased; the fruit is tolerably rich in fat; the whole young foliage of the potato belongs to those vegetables which are richest in nitrogen, the proportion of the dry substance amounting to 7·5 per cent. = 47 per cent. crude proteïn; the amount of nitrates in the non-proteïn portions is also very considerable, in the whole plant 3·5 per cent., in the stalks 5 per cent., calculated as N_2O_5.

This large quantity of nitrates leads the author to agree with André, Berthelot, and Schulze, that it is not altogether supplied from external sources, but that a part is formed in the plant itself. J. F.

Ammonia in Beetroots. By L. Battut (*Bied. Centr.*, 1886, 604—607).—The opinions of persons who interest themselves in this matter are divided, some asserting the presence of ammonia in the roots, others the contrary. Owing to the rapid decomposition of the organic constituents of beet-juice when heated with alkalis, the deter-

minations were made in the cold by Schlösing's method—in each of four dishes 100 c.c. of distilled water was poured, in one normal beet-juice with 10 c.c. milk of lime, in two others milk of lime with two kinds of ammonium salts, the fourth milk of lime only—the dishes covered with glass plates to which were fixed moistened test-papers; the three gave an immediate alkaline reaction. Attempts at quantitative estimations were made without much success, but the author concludes from their results that an ammoniacal salt exists in the roots which is readily decomposed by caustic magnesia, and that there are two nitrogenous organic substances present, one, probably asparagine, quickly decomposed by lime, the other by caustic potash solution.

J. F.

Milky Juice of Certain Euphorbiaceæ. By G. Henke (*Arch. Pharm.* [3], **24**, 729—759).—Hitherto euphorbone had not been obtained in a pure state, even Flückiger, who proposed the name, was unsuccessful. The author treated finely powdered euphorbium in the cold with light petroleum of 60—70° boiling point; this treatment being repeated as long as anything was dissolved. The solutions obtained were mixed, filtered, and allowed to evaporate spontaneously. The sides of the evaporating vessel became coated with beautiful, transparent, crystalline needles of euphorbone, whilst the remainder of the residue consisted of a yellowish, crystalline, warty mass. Repeated treatment with light petroleum gives a pure product finally, but is wasteful; it is better to dissolve the yellow mass in ether after removing the petroleum by heating on the water-bath; on adding alcohol until a faint turbidity appears, filtering and allowing to remain, a yellow, resinous mass separates. The liquid on evaporation leaves a snow-white, butter-like mass which gives brilliant needles on crystallising from a sufficiently dilute solution of light petroleum. *Euphorbone* thus prepared melts at 67—68°, its composition was found to be $C_{20}H_{36}O$. Its rotatory power dissolved in chloroform was $[\alpha]_D = + 15{\cdot}88°$. Its crystals are persistent in the air, tasteless, and are neutral in solution. It is very soluble in light petroleum, chloroform, ether, alcohol, benzene, acetone, and 90° vol. per cent. alcohol, less soluble in more dilute alcohol. It is unaffected by dilute acids, sodium carbonate, ammonia, potash, and soda, and by alcoholic zinc chloride solution. It is soluble in 10,000 parts of hot water. Cold anhydrous acetic acid does not affect it; when heated at 150—200° a solution is obtained from which a yellowish precipitate is thrown down on diluting with much water, this precipitate has the properties of unchanged euphorbone. Bromine acts violently on the compound, producing a yellow, resin-like, non-crystallisable mass. Hot nitric acid dissolves euphorbone, and from the solution an amorphous, nitrogenous compound can be obtained. A granular oxidation product was obtained by long boiling with potassium dichromate and sulphuric acid. On heating euphorbone with phosphoric anhydride, heptane, octane, xylene and small quantities of other aromatic hydrocarbons were obtained. The residue from the preparation of euphorbone, when extracted with alcohol, yielded two resins, one soluble and the other insoluble in ether; their reactions are detailed. The detection of malic acid, gum, and other substances in the residue and the extrac-

tion therefrom are described. The pure euphorborium was found to contain:—Euphorbone, 34·60; resin soluble in ether, 26·95; resin insoluble in ether, 14·25; caoutchene, 1·10; malic acid, 1·50; gum and salts precipitated by alcohol, 8·10; gum and salts not precipitated by alcohol, 12·30; salts and organic substances soluble in ammonia, 1·20 per cent. Somewhat similar results were obtained in the case of juices of other plants of the euphorbia class. J. T.

Composition of Barley and Pease. By Klien (*Bied. Centr.*, 1886, 644—645).—The author's experiments show that in soils containing but little lime, large quantities of superphosphate diminish the proteïds contained in the grain, whilst soils rich in lime bear very heavy manuring with those substances without damage to the crop; precipitated phosphate, a neutral combination of phosphoric acid, was applied in considerable excess without reducing the proteïds; even in a soil composed of phosphorite containing 20 per cent. of phosphoric acid, the proteïd was not lower in the case of pease than in normally manured soils. Wagner has found that an increase in proteïd by heavy manuring with phosphates can only be obtained in straw and green crops, not in grain and seeds, the percentage being diminished in the latter by large applications of phosphatic manures; the author thinks Wagner's conclusions are true only when the soil is poor in lime and has traces of mineral acids present, in such cases he recommends the application of neutral, that is, precipitated phosphate.

J. F.

Composition of Tea-leaves. By O. Kellner (*Landw. Versuchs-Stat.*, 1886, 370—380).—The chief interest in this research lies in the fact that it is almost the only case in which an evergreen plant has been systematically examined throughout the year. The leaves were dried at 60—80°, and the "total nitrogen" estimated by soda-lime, whilst the albuminoïd nitrogen was determined by a modification of Stutzer's process, because theïne-tannate is only decomposed with difficulty and at 100°; also the filtration of the solution is attended with great difficulty. The method employed was to boil 2 grams of the substance with 100 c.c. water, to add 20 c.c. of a 10 per cent. copper sulphate solution, and then to precipitate the copper by a titrated solution of sodium hydroxide, still leaving a small quantity of copper in solution; after washing with hot water, the precipitate was washed with 95 per cent. alcohol. The filtrate ran rapidly through the paper and was free from albuminoïds, which were found to be rather lower than the original process showed. The total soluble matter was estimated indirectly, in that 3 grams were repeatedly boiled with water, the residue being dried and weighed. Theïne was estimated in 5 to 7 grams which were boiled in water, the solution evaporated, and *magnesia usta* added; after gently drying, the residue was extracted with ether, and the alkaloïd obtained by evaporation. To obtain the tannic acid, which by reason of the presence of pectin could not be filtered in the usual way, the leaves were extracted with alcohol acidified with a few drops of acetic acid, the solution thus obtained evaporated and the residue dissolved in water, and filtered through asbestos: in calculating the results, 63 parts of oxalic acid were taken

Date.	Water in fresh leaves.	Percentage on Dry Matter.											
		Crude proteïn.	Crude fibre.	Ethereal extract.	Cellulose, &c.	Ash.	Theïne.	Tannin.	Soluble in hot water.	Total N.	Album. N.	Theïne N.	Amido N.
May 15	76·83	30·64	9·10	6·48	49·09	4·69	2·85	8·53	36·18	4·91	3·44	0·81	0·66
„ 30	75·78	24·25	17·25	6·42	47·32	4·76	2·80	9·67	37·17	3·88	2·77	0·79	0·32
June 15	78·61	22·83	17·38	6·65	48·26	4·88	2·77	10·10	36·12	3·65	2·73	0·78	0·14
„ 30	70·85	21·02	18·69	6·83	48·50	4·96	2·59	10·25	36·06	3·37	2·43	0·73	0·21
July 15.....	72·67	20·06	19·16	7·00	49·49	4·29	2·51	9·40	31·72	3·21	2·31	0·71	0·21
„ 30.....	70·54	19·96	17·56	8·59	49·43	4·46	2·30	10·44	33·77	3·19	2·25	0·65	0·29
August 15	64·21	19·05	17·72	10·85	47·80	4·58	2·30	10·75	32·70	3·05	2·28	0·65	0·12
„ 30	67·75	18·58	17·95	12·14	46·35	4·98	2·22	11·09	34·00	2·91	2·19	0·63	0·16
September 15....	65·26	18·27	19·13	13·40	44·35	4·85	2·05	11·32	30·01	2·93	2·27	0·59	0·08
„ 30....	64·20	18·15	19·17	14·16	43·41	5·11	2·06	10·91	33·05	2·91	2·39	0·58	—
October 15.....	64·66	17·91	18·66	17·23	41·14	5·06	1·83	11·21	34·76	2·87	2·45	0·52	—
„ 30.....	64·11	17·98	18·40	19·50	39·05	5·07	1·79	11·27	36·80	2·88	2·35	0·51	0·02
November 15 . ..	59·43	17·70	18·26	20·38	38·66	5·00	1·30	11·34	38·21	2·83	2·30	0·37	0·16
„ 30	60·97	17·14	18·34	22·19	37·31	5·04	1·00	12·16	37·91	2·74	2·35	0·28	0·11
May 15 ..... (old leaves).	60·03	16·56	17·62	14·18	46·50	5·14	0·84	11·11	36·45	2·67	2·43	0·23	0·01

In 100 *parts of Pure Ash.*

Date.	K_2O.	Na_2O.	CaO.	MgO.	Mn_3O_4.
May 15	49·06	1·07	11·95	8·69	1·64
„ 30	46·33	2·00	14·93	9·00	1·79
June 15	41·37	1·23	17·70	11·72	1·98
„ 30	37·09	1·59	21·95	11·67	1·30
July 15	35·76	1·58	22·04	12·21	1·58
„ 30	32·84	0·80	22·88	12·91	1·75
August 15	31·01	1·08	23·24	13·71	1·21
„ 30	29·15	1·14	22·20	14·79	1·57
September 15.....	23·72	4·77	23·44	14·74	1·72
„ 30.....	22·28	2·06	27·71	15·80	1·63
October 15.....	20·97	2·76	27·90	15·88	1·37
„ 30.....	19·75	2·72	28·75	17·19	1·53
November 15.....	18·67	2·76	29·60	17·39	2·06
„ 30.....	17·31	2·02	30·37	17·99	2·48
May 15 (old leaves)...	14·20	3·21	30·46	18·49	2·82

Date.	Fe_2O_3.	P_2O_5.	SO_3.	SiO_2.	Cl.
May 15	3·80	16·67	3·75	2·34	1·04
„ 30	4·30	15·63	3·61	1·24	1·39
June 15	6·55	13·76	3·21	1·60	1·06
„ 30	7·25	13·35	3·56	1·41	1·18
July 15	8·48	12·41	3·37	1·62	1·17
„ 30	9·75	12·33	3·83	1·35	1·22
August 15	12·14	12·00	3·43	1·02	1·14
„ 30	11·02	11·71	3·81	2·72	1·13
September 15.....	11·64	11·25	4·74	1·69	1·58
„ 30.....	12·11	11·52	4·08	2·17	1·35
October 15.....	11·83	10·71	4 37	2·61	1·11
„ 30.....	11·63	10·23	4·01	2·44	1·38
November 15.....	11·37	10·70	3·84	1·75	1·09
„ 30.....	11·02	10·96	4·02	2·70	1·19
May 15 (old leaves)...	11·93	10·64	4·41	2·13	1·32

to be equivalent to 34·25 gallotannic acid; the tannin in tea being identical with that acid. The composition of the leaves is shown in the accompanying tables.

The fluctuation in the percentage of water is less than that observed in leaves of deciduous trees; the percentage of ash lies between that found in the needles of pines and in ordinary leaves. It will be noticed that the non-albuminoïd nitrogen is almost wholly absent during the later stages of growth, being found as theïne. Connecting this with the fact that albumin has increased, and that no theïne is found in the seeds, the author believes that positive proof is afforded that the alkaloïd, like glutamine and asparagine, is a decomposition product of albumin, and is capable of again forming albumin.

As regards the ash, we have here a regular increase, whilst in deciduous trees is found both diminution and increase. E. W. P.

China bicolor. By O. Hesse (*Annalen*, **234**, 380—384).—The author is of opinion that the small quantities of quinine and other alkaloïds which Hodgkin (*Pharm. Jour.*, **15**, 217) found in the bark of *China bicolor*, are probably due to the presence of a small quantity of the bark of *Remijia pedunculata* in the *China bicolor* bark.

W. C. W.

Chlorosis in Plants. By J. v. Sachs (*Bied. Centr.*, 1886, 602—604).—When attacked by this disease, the leaves pale and turn perfectly white; weak plants succumb quickly. Stronger ones are attacked year after year until their reserve material is exhausted; they then die. The touching of a diseased leaf with a dilute solution of an iron salt often causes the production of chlorophyll and cures the disease. However, from extended observations the author does not think that it is altogether the absence of iron that causes the disease, as plants growing on the same soil are irregularly attacked, some escaping altogether. His experience leads him to think that the roots or leading vessels suffer some alteration which prevents the minute quantities of iron contained in the sap from reaching the leaves. A too rapid and luxuriant growth favours the disease. In the winters of certain years, thousands of trees and shrubs were heavily pruned; the energy divided between numerous growths was concentrated on a much less number; they grew rapidly and luxuriantly; the first leaves were green, but the later were quite white. Trenches 20 to 30 cm. deep and wide were dug round the diseased trees at a distance of 80 to 100 cm.; in these trenches ferrous sulphate in lumps was placed, in quantities varying from 1 to 5 kilos., according to the size of the tree. Water was then freely admitted and the trenches filled up with earth. Within three to six days the smaller bushes commenced to green, within 14 days no sign of chlorosis was visible, and in the following spring all the growths were normal.

An experiment of the author's has, he considers, an important bearing on vegetable physiology. Certain acacia trees showed symptoms of chlorosis, in particular the thick branches of a 20 year old tree. The author caused holes to be bored in the main stem, just beneath the bifurcation of the branch with the core of the tree. In these holes he placed corks fitted with funnels, charged afterwards with ferrous sulphate or ferric chloride in dilute solution. In dry weather the tree absorbed the solutions so readily that the funnels had to be frequently refilled. The leaves in line of each funnel became quite green in 10 to 14 days, but those not in the line remained white. This the author thinks a proof that each branch and twig has its own sap-ducts.

J. F.

Absorption by Soils. By O. Kellner (*Landw. Versuchs-Stat.*, 1886, 349—358).—After a detailed description of the modification of Pillitz's method, which was employed to estimate the absorption of various solutions by soils, the author shows that the absorption of bases by the soils he employed is but slightly dependent on the composition of those soils; that soils rich in zeolites and humus have not of necessity a higher absorptive capacity; nor does absor-

tion wholly depend on the quantity of the absorbing medium, but largely on the character of the surfaces with which the absorbable substances come in contact. It would appear also, that potash and ammonia are absorbed according to the ratio of their equivalents. E. W. P.

Estimation of Absorbed Bases in Soils, &c. By O. Kellner (*Landw. Versuchs-Stat.*, 1886, 359—369).—From the analytical details given, it is concluded that the potash held in a soil by absorption only may be readily estimated by digestion of the soil in a concentrated solution of ammonium chloride. As regards the estimation of lime, the author has failed, as the soils he employed would not retain added lime. He attempted to saturate with calcium chloride and then remove with ammonium chloride, but found more lime present in the solution than should have been, showing that other forms of lime (carbonate) had been attacked. In a second series of experiments, he found that peas, when growing, only assimilated the potash and lime held in solution in the soil, and that the insoluble compounds (anhydrous silicates, &c.) were in no wise taken up by the roots. E. W. P.

Chili Saltpetre as Manure. By A. Stutzer (*Bied. Centr.*, 1886, 585—597).—The author was awarded the first prize offered by the union of nitrate firms on the western coasts of South America, for his essay on the value of Chili saltpetre as a manure. Wagner has condensed the contents of this essay and that of Damseaux, which obtained the second prize, into a compact form of questions and answers, which are of value in agricultural science. Some of the answers follow :—Plants cannot grow under normal conditions unless a supply of nitrogen is available for their roots, and a satisfactory crop cannot be obtained without the use of nitrogenous manures. Stable manure, in the quantities produced on a farm, does not provide sufficient nitrogen to produce good results; high farming requires that nitrogen be procured as artificial manure. Manures containing nitrogen in the form of animal matter take a long time to alter into nitrates, whilst the Chili saltpetre is at once available.

The increase in weight of various crops tried was greater when the saltpetre was used than when ammonium sulphate was the manure. The application of phosphates and potassium salts increase materially the activity of the saltpetre. This manure does not unduly exhaust the soil; it renders the mineral plant foods more assimilable, but no more of them is removed than is accounted for in the increase of the crop. The crops which are most benefited by Chili saltpetre are all straw-growing plants; next rape, mustard, &c.; fodder, sugar-beets and potatoes come in the second rank; meadow grasses in the third; the least effect is produced on pease, vetches, lupines, clover, and linseed. Chili saltpetre should be applied as top-dressing only on sandy or porous soils, just before vegetation begins; the time of application should be in early spring. J. F.

Comparative Manurial Values of Chili Saltpetre and Ammonium Sulphate. By v. Magerstein (*Bied. Centr.*, 1886, 583—585).

—The experiments were made on a sandy soil, with barley and oats. 200 kilos. of Chili saltpetre and 300 kilos. of ammonium sulphate were used to the hectare; the plots manured with the former salt showed a better result in grain, but a smaller yield of straw. Compared with unmanured plots, the increase obtained by manuring was—

	Barley.	Oats.
Chili saltpetre	8·13 hect. grain.	10·25 hect. grain.
Ammonium sulphate....	5·46 „	6·94 „

Calculating the cost of the manures and the market prices of barley, oats, and straw, the author considers the Chili saltpetre the more paying of the two. J. F.

Experiments with Chili Saltpetre. By v. Magerstein (*Bied. Centr.*, 1886, 581—583).—In order to compare the effects of this manure when used as top-dressing and when dug in, the author prepared plots of 7 to 8 square metres all cultivated in the same way, except as regards the application of the manure. In the cases of potatoes and oats, the top-dressing gave the better results, but the contrary was the case with barley: the difference is attributed to the dryness of the season. The solution of the salt was slow and concentrated; therefore unfavourable to growth. The roots of barley came first in contact with it, whilst the deeper roots of potatoes and oats received a more dilute solution and were stronger when it reached them. J. F.

Analytical Chemistry.

Kjeldahl's Method of Estimating Nitrogen. By C. Arnold (*Arch. Pharm.* [3], **24**, 785—794).—The author shows that this method (Abstr., 1884, 364; 1885, 930) is also applicable to nitrates, nitro- and cyanogen-compounds, in the presence of benzoic acid, sugar, mercury, and copper sulphate; further, in the case of alkaloïds and other compounds that can be treated by this method, oxidation by potassium permanganate is unnecessary if the boiling be continued until the warm liquid acquires a bluish-green tint, becoming colourless on cooling; this takes place tolerably quickly in the presence of mercury and copper. That the oxidation has been completed can readily be ascertained by adding a crystal of potassium permanganate, which should give a persistent violet or green coloration. A description of the apparatus used by the author is given. J. T.

Separation of Arsenic and Antimony. By Zambelli and Luzzato (*Arch. Pharm.* [3], **24**, 772).—These elements can be separated, even in forensic cases, by treating the still moist sulphides with hydrogen peroxide at 40° for some hours, then heating to near 100°

and filtering. The arsenic acid formed goes into the filtrate, whilst the insoluble antimony oxide remains on the filter. The method is said to be very delicate. J. T.

Detection of Thiosulphate in Hydrogen Sodium Carbonate. By Brenstein and T. Salzer (*Arch. Pharm.* [3], **24**, 761).—According to Brenstein, the reaction given for thiosulphate by Mylius is not characteristic, as other oxygen-compounds of sulphur, such as sulphites, give rise to the formation of hydrogen sulphide. A better test for thiosulphate is to add to a 5 per cent. solution of hydrogen sodium carbonate a few drops of silver nitrate solution, then excess of nitric acid, and heat to boiling; even minute traces of thiosulphate give an immediate dark precipitate of silver sulphide.

According to Salzer, the absence of thiosulphate is easily ascertained by adding a few drops of iodine solution to about 20 c.c. of a saturated solution of hydrogen sodium carbonate; the solution must have a yellowish tint. Decolorisation of the iodine solution does not necessarily imply the presence of thiosulphate, since normal carbonate, the most commonly occurring impurity, produces this effect. Both authors found thiosulphate to be a constant impurity of ordinary qualities of hydrogen sodium carbonate, whilst the better qualities were mostly free from it. J. T.

Estimation of Small Quantities of Silver in Burnt Pyrites. By E. Thilo (*Chem. Zeit.*, **10**, 822; 1065—1067).—The amount of silver in burnt pyrites is ordinarily 0·003—0·008 per cent., and to obtain trustworthy results material containing 0·01 gram of silver should be taken for analysis, or about 300 to 500 grams of pyrites. Many difficulties have been encountered in endeavouring to deal with these large quantities of material so as to get all the silver. Experiments show that the decomposition of the whole mass is out of the question, therefore methods for extracting the silver, &c., were tried; treatment with nitric acid or with gaseous chlorine, and subsequent extraction of the silver chloride proved unsuitable. Digestion with chlorine-water was somewhat better; but bromine or bromine-water gives the best results. The powdered burnt pyrites is passed through a 0·25-mm. mesh sieve, and about 300—500 grams of it is placed in an acid-proof iron basin; it is well covered with water, and while vigorously stirred, bromine is added until present in excess. After 24 hours it is heated on a water-bath for one hour with frequent stirring, treated with excess of ammonia, then with 500 grams of ammonium chloride, and 1 litre of water. The mass is boiled for an hour, and filtered. The residue is dried, ignited at a low red heat, and again treated with ammoniacal ammonium chloride, by which means all the silver is extracted. Inasmuch as copper is quite as difficult as silver to extract by means of bromine, and as the amount of copper in the pyrites is reduced from 5 per cent. to a trace (0·01 per cent.) by the above treatment, this may be used as an indicator of the progress of the desilvering, and in practice when the copper is reduced to this amount it may be safely inferred that all the silver is removed. The solution, about 4 litres, is made acid with hydrochloric acid; it is not

affected by daylight either before or after acidifying. The silver, copper, and lead are then precipitated by means of chemically pure zinc. When the precipitation is complete, the solution is colourless (or rose-red if cobalt is present), and is not turned blue by ammonia. As the precipitate contains, most likely, silver chloride and bromide, and some iron oxide, it is fused with potassium cyanide, and subsequently with anhydrous borax, the temperature being raised to melt the copper. The regulus is dissolved in nitric acid, and the silver either precipitated by means of hydrochloric acid or determined electrolytically. Silver determinations may also be made in ordinary pyrites, which is first roasted carefully, and then treated in the above manner. Good results have been obtained by this method, with roasted copper schist, with spathic iron ore containing argentiferous tetrahedrite and pyrites, and with other ores. A determination can be completed in three days. D. A. L.

Comparative Gasometric Assaying with Especial Reference to the Valuation of Zinc Powder and the Testing of Carbonates. By J. Barnes (*J. Soc. Chem. Ind.*, 5, 145—147).—In a previous communication (Trans., 1881, 462), the author described a method for the valuation of zinc powder, consisting in measuring the amount of hydrogen liberated on treatment with an acid. The author has since devised a method and constructed an apparatus for gasometric assaying, contrived originally for the valuation of zinc powder, but applicable also to the estimation of other substances, which may be made to cause or control the evolution of gases. The method, which is described in detail in the paper, is a comparative one, and requires at least two graduated instruments, each provided with a suitable gas evolving arrangement. A substance of known value, taken as the standard, is placed in one, and the sample to be examined in the other instrument. The value of the sample is then calculated by the following formula: $\frac{v}{V} \cdot \frac{W}{w} \cdot R = x$; where V equals the volume of gas from standard, v the volume of gas from sample, W the weight of standard, and w the weight of sample. R is the amount of pure substance or its equivalent in unit of standard, and x the amount of pure substance in unit of sample. D. B.

Determination and Valuation of Copper in Ores and Products for Commercial Purposes, with some Remarks on the Assay of Gold in Bar Copper. By J. W. Westmoreland (*J. Soc. Chem. Ind.*, 5, 48—64).—*Estimation of Moisture.*—This, although apparently a simple process, is conducted very differently by various assayers, and the author proposes that the temperature and manner in which the moisture is to be taken should be more clearly defined than it is at the present time.

Wet Assay of Copper.—Having examined a large number of samples of all kinds of copper ores and products by several wet processes, the author has given the iodide process as modified by Brown the preference—being more trustworthy and accurate than the electrolytic process. For cupreous pyrites, burnt ores, &c., the following method

may be used. From 50 to 150 grains of the sample is dissolved in acids, evaporated to dryness with excess of sulphuric acid, diluted with water and filtered. From this solution, the copper is separated with sodium thiosulphate, the precipitate dried, ignited, dissolved in nitric acid, evaporated with sulphuric acid to separate traces of lead, diluted with water and filtered, sodium carbonate added in excess, and then acetic acid to acid reaction. The solution is then titrated with potassium iodide. As an alternative method, the ore may be calcined, dissolved in hydrochloric acid, the ferric salt reduced by boiling with a solution of sodium sulphite, and hydrogen sulphide passed through the cold solution; the precipitated sulphides are then washed, and the process conducted as before. Richer copper ores, mattes, precipitates, &c., are dissolved in acids, and the solution precipitated either with sodium thiosulphate or hydrogen sulphide, the sulphides being dissolved in acids, and treated as before. The accuracy of this process was tested by numerous experiments, in which known weights of pure electrotype copper, silver, arsenic, antimony, lead, cadmium, bismuth, tin, manganese, zinc, and iron salts were used. The solutions were made to represent cupreous burnt ores, mattes, cupriferous lead regulus, second quality and rich precipitates, &c. Experiments were also made in many cases with the metals separately. The electro-deposition method may be employed in cases where it is desirable to have results of two separate and distinct processes, it being noted that with pure solutions of copper, accurate results are obtained, whilst when silver or bismuth are present they are precipitated, and in one experiment tin was also deposited with the copper. In the presence of ferric salts, the deposition is retarded. It was found that whilst the results with refined or bar coppers and rich precipitates agree with those obtained by the iodide process, those obtained by electrolysing sulphuric acid solutions of mattes, copper ores, &c., are generally slightly below the true percentage. With burnt ores, cupreous pyrites, and ores containing but little copper, the author first precipitates with hydrogen sulphide, dissolving the sulphide in nitric acid, and evaporating this solution with excess of sulphuric acid, the sulphates dissolved in water give a solution from which copper (and bismuth) is readily deposited. The results by the battery process are generally from 0·01 to 0·04 per cent. higher than by the iodide process, this being caused by a slight deposit of bismuth.

The Cornish Process of Dry Assay.—This process is considered to be inaccurate and misleading, and is also liable to serious variation even in the hands of experienced operators.

The author is of opinion that in cases where the sulphur contents of pyrites are sold to alkali works, the burnt ores being returned to the vendors, an accurate wet assay forms the best check on the copper contents of the ore delivered to and received from the alkali works.

In the remaining part of the paper, the methods in vogue for fixing the prices payable for copper in pyrites, copper ores, &c., are discussed. Reference is also made to the assay of gold in bar copper, and the opinion is expressed that these assays are not conducted as carefully as they should be, taking the value of the metal into consideration.

D. B.

Estimation of Ammoniacal Nitrogen in Soils, and the Amount of Assimilable Nitrogen in Uncultivated Land. By A. Baumann (*Landw. Versuchs-Stat.*, 1886, 247—303).—The methods employed to estimate the ammonia in soils are unsatisfactory. Schlösing's method, whereby the ammonia is freed by means of milk of lime or sodium hydroxide, gives results too high, probably owing to the formation of ammonia from other compounds during the period (2—3 days) required for the process. In Boussingault's process as modified by Schlösing, a hydrochloric acid extract of the soil is treated with magnesia usta, but the ammonia collected in acid must not be estimated by titration, but must be azotometrically determined; nor must cork nor caoutchouc be employed in the formation of the apparatus. The liquid in the evolution flask must be boiled for at least an hour, and the magnesia usta must be fresh. With these two processes, it is found that humous soils, when treated with sodium hydroxide, continuously yield ammonia; if the soil, after treatment with magnesia, be further treated with sodium hydroxide, another supply of ammonia is obtained, but only in the case of soils rich in numus. Knop's process, in which the ammonia is decomposed by brominated sodium hydroxide solution, is vitiated by the fact, noticed by Knop and others, that in the presence of the soil itself a contraction of the volume of gas enclosed in the apparatus occurs; this contraction was stated by some to be due to absorption by the organic matter, whilst others considered the oxides of iron in the clay to be the real cause; also it had been stated that the presence of borax prevented this contraction. To ascertain the cause of the contraction, a sample of stiff soil poor in humus, was taken from uncultivated land at a depth of 15—20 cm.; this sample seemed free from humus, although root-fibres were visible; at a distance of 40 m. from this spot another sample was drawn from a depth of 2—10 cm., this was close to a pine 50 years old. The sample showed humus, and when dry was grey. At another spot, close to a 100 year old pine, a third sample was taken, and this when dry was dark-brown. These last two samples overlaid a soil similar to the first sample. Employing these samples, the author argued that if the contraction was due to the clay and the iron, and not to the humus, then identical contractions would be observed when equal quantities of all samples were subjected to like conditions. On the other hand, if the phenomenon is caused by the humus, then that sample richest in humus would produce the greatest effect on the volume of the gas, and when borax was employed no contraction should occur. It appears that the ferruginous soil poor in humus produced no contraction, but rather an increase of volume after the first $\frac{1}{4}$ hour; this is explained by the probable presence of nitrogenous matter decomposable by the brominated alkali. The presence of borax assisted the evolution of gas.

Experimenting with humous samples, it was found that the volume of gas evolved by Knop's method stands in no ratio to the percentage of ammonia present; this remarkable result was most manifest in the case of the third sample, which contained most humus, for then the contraction was evident when only 5 grams were used,

and in spite of borax the contraction amounted to 71 per cent. when 100 grams was employed. This contraction is clearly due to oxidation of the organic matter of the soil, and consequent removal of part of the gaseous contents of the azotometer.

Working with sandy and chalky soils, the author found that the results obtained by Knop's method are quite as untrustworthy as in the case of humous samples.

The following method is recommended for the estimation of ammonia in soils:—200 grams of the soil is mixed with 100 c.c. of hydrochloric acid (1 : 4), then diluted with 300 c.c. of distilled water and allowed to remain for two hours, with frequent shaking. Should much chalk be present, then more than 100 c.c. acid must be added, and the whole amount of *liquid* made up to 400 c.c.; all heating must be avoided. Of the filtrate, 200 c.c. (= 100 grams soil) is placed in the evolution vessel of the azotometer together with 5 grams of freshly ignited magnesia usta, and the vessel closed by a doubly bored india-rubber stopper; through one of the borings a glass tube passes to the bottom of the flask, whilst the other opens immediately below the stopper, and is connected with an aspirator, whilst the other tube supplies air ozonised by passing through potassium permanganate and concentrated sulphuric acid. The passage of this gas for 10 minutes oxidises organic matter, so that no subsequent contraction occurs. The rest of the process is conducted in the ordinary way.

Percentage of Ammonia in Soils.—Soils of various characters were examined, and the percentages as found by Schlösing's and the other methods are given: there appears to be a wide difference between the first and the other two methods. The percentages at different periods in summer and at different depths are recorded. The conclusions drawn are that the percentage of ammonia in uncultivated soils varies with the character of the soil, loams containing most, the quantity increasing with the increase of clay; chalks and sands are poor in ammonia, but in sands rich in humus there is a large supply of organic compounds which readily decompose and yield ammonia, although generally speaking, the percentage of organic matter is no indication of the amount of ammonia present, and the percentage of ammonia in a soil does not seem to vary with the weather, but does decrease with depth from the surface.

Percentage of Nitrates in Unmanured Soils.—Baumann employs Schlösing's method of estimating nitrates if the solution of 1000 grams soil in water made up to 2000 c.c. shows the brucine reaction, even if the reaction is only obtained after evaporating the solution to one-half of its original volume. If this test should fail, then diphenylamine is to be employed; this should indicate 1 in 1,500,000 or 0·6—1 mgrm. per litre; should this fail, so also will Schlösing's method, and it will be necessary to evaporate 1 litre of extract with some alkali to dryness, add alcohol, boil, filter, and then evaporate the alcohol and dissolve in 40 c.c. water. The solution must be again tested by brucine and diphenylamine, and if indications of the presence of nitrates are visible, the Marx-Trommsdorf's method (*Zeit. anal. Chem.*, 1868, 412, and 1870, 171) is to be employed for the quantitative

estimation; this will indicate 0·00001 per 300—400 grams soil. Examination of many soils shows that when the soil is uncultivated the percentage of nitrates is very small, especially in forests, where it only appears as traces.

The author then reviews the work of Warington, Schlösing, and Müntz on nitrification, and considers that the absence of nitrates in such soils as he refers to, is due to the normal temperature (5°) being so close to that at which nitrification first occurs; also water is necessary for nitrification, and in forest soils, therefore little nitrification takes place, because of the great dryness of that soil in summer, due especially to the enormous transpiration continually occurring, which renders the soil almost "air-dry;" a further cause for the absence of nitrification may be found in the want of animal nutriment for the growth of the ferment. E. W. P.

Analysis of Gas Coal. By L. T. Wright (*J. Soc. Chem. Ind.*, **4**, 656—667).—*Proximate analysis.*—The first determination is that of moisture. Various temperatures have been recommended at which the sample of coal shall be dried. Since 100° is a temperature easily secured and maintained constant by means of a water-bath, the author has adopted it as the standard. The estimation of moisture by loss of weight in drying at 100° until the weight of the substance becomes constant is not, however, free from error; as it has been noticed by different observers, that after a time the coal not only ceases to lose weight but actually gains. Hinrichs attributes this increase to the slow oxidation of pyrites and other substances in the coal; the author, however, considers it to be due to the absorption of gases into the pores of the coals left vacant by the expelled moisture. He has also found that the increase of weight, which only exhibits itself when the coal has been nearly dried, has been going on during the whole period of the drying process, so that where accuracy is required it is preferable to weigh the water as such. According to Hinrichs the total volatile matter of coal is determined with accuracy by taking 1 to 2 grams of undried pulverised coal, heating for three and a half minutes over a Bunsen burner, and then immediately igniting without cooling, for the same period over a blast gas lamp (white heat). The greatest difference which Hinrichs obtained amounted to 0·29 per cent. The author has repeated this method and obtained very fair results, although not quite so accurate as the above. The author adopts the following method:—Take about 2 grams of finely pulverised coal and let it form an even layer on the bottom of a thin platinum crucible. Weigh without cover, place the crucible (with cover on) in an upright position, then apply a powerful gas flame. Note when the gases cease issuing from under the lid; allow one minute further heating, remove the gas flame, place the crucible and cover in a desiccator for about five minutes to cool, and then weigh without cover as soon as possible. For the determination of ash in refractory cokes and such substances as gas carbon, heat to redness 2 grams of the coal or coke placed on a piece of platinum foil, in a combustion tube through which a gentle current of air is drawn. The ash should be saved for the determination of sulphuric acid.

For the determination of the total sulphur, the best and simplest method is that suggested by Nakamura, which consists in heating the coal below a red heat in contact with alkaline carbonates, when the coal whether bituminous or not rapidly undergoes complete oxidation. For the purpose of distinction between the sulphur which goes over into the volatile matter, the sulphur left in the coke and that which is finally left in the ash combined as sulphate, three determinations are required :—(1) Total sulphur by Nakamura's method. (2) Sulphur which is converted into sulphurous anhydride by combustion of the coke in air, obtained by roasting a quantity of coke representing a known quantity of the coal, and aspirating the gaseous products of combustion through a solution of iodine or bromine. (3) Sulphur in ash. This can be done either by boiling the ash with hydrochloric acid, filtering and determining the sulphuric acid in the filtrate, or by fusion with alkaline carbonates.

Proximate Analysis of Australian Shale.

Sp. gr. = 1·0401.

Water lost at 100°	0·44	—
Volatile matter	77·69	Corrected for sulphur.
Fixed carbon	5·56	„ „
Ash	15·83	„ „
Sulphur in volatile matter....	0·48	0·4548
„ fixed carbon		0·0121
„ ash.....		0·0137
	100·00	

The practical method of examining coal for gas-making purposes partakes of two forms : (1) a partial imitation of the process of gas manufacture on a small scale ; (2) analysis of coal by conducting a gas manufacture in a setting of clay retorts with large plant for exhausting, condensing, scrubbing, purifying, measuring the gas, and so on, as is in actual use.

The laboratory practical analysis is undoubtedly of great value ; it will, however, be necessary in interpreting the results, to recollect that the method of heating the coal is different to that used in practice with clay retorts. As far as quality and volume of gas are concerned, the best results are obtained with the small iron retort. The difference varies with the kind of coal employed. With the very finest coking coals the difference is very small, and as the coking quality of the coal increases so the difference between the two methods of testing increases. With coals (not cannels) which scarcely intumesce at all, the difference becomes very high. Cannels also vary in the same manner, the difference in the results being always connected with differences in the qualities of the cokes. Since the gas from the iron retort is not scrubbed, a deduction of about 3 per cent. should be made from the results of the small apparatus to compensate for the small loss of illuminating power suffered by the gas

of the large experimental works in the washing process. When this allowance is made there is but little difference between the two methods of testing in the case of coking coals.

Estimation of Hydrogen Sulphide and Carbonic Anhydride in Crude Coal-gas.—The author prefers the use of a method admitting of the employment of a tolerably large quantity of gas collected regularly during an interval of time sufficiently long to afford an idea of the average composition of the gas supply to be tested. The reagent used for absorbing the hydrogen sulphide is cupric phosphate. Absorption tubes charged with cupric phosphate gain in weight under the action of pure coal-gas; the increase of weight, however, soon reaches a limit, and the phosphate may be saturated by passing 3 cubic feet of pure dry-coal gas slowly through the tubes. The carbonic anhydride is absorbed in soda-lime tubes, one half full of soda-lime and one half of calcium chloride. To increase its absorptive power for carbonic anhydride the soda-lime is used in a moist condition. In cases where ammonia exists in the gas its removal is best effected by passing the crude gas before it is dried through a 12-inch U-tube filled with broken pumice saturated with syrupy phosphoric acid.

Cyanogen.—This substance is estimated by passing a measured quantity of crude gas freed from ammonia through a U-tube filled with soda-lime, and then making a combustion of the residue as in an ordinary nitrogen determination. D. B.

Analysis of Explosives. By G. Lunge (*Chem. Ind.*, **9**, 273—274).—To render the author's nitrometer suitable for the determination of nitrogen by Crum's method in substances like dynamite and gun-cotton, which cannot be introduced into the decomposition tube in the liquid form, and at the same time to avoid the error due to the evolution of carbonic anhydride to which Hempel's modification (this Journal, **40**, 472) is liable, a small funnel-tube bent into a swan-neck is fitted by a rubber stopper to the cup in which the weighed substance has been placed. Through this the sulphuric acid required to dissolve the substance is poured. Any carbonic anhydride evolved can escape, but loss of nitrous fumes is prevented by the acid which remains in the bend of the swan-neck. When the substance has dissolved (which in the case of gun-cotton may take three-quarters to one hour) the solution is drawn into the graduated tube. The acid in the funnel tube follows and rinses the cup. The stopper can now be removed and further rinsings given. The siliceous earth suspended in the acid has not been found to cause any inconvenience. Three analyses of gun-cotton reported agree very closely. M. J. S.

Estimation of Glycerol in Wine. By Samuelson (*Chem. Zeit.*, **10**, 933—934).—Great discrepancies are observed in the estimation of glycerol by different chemists; this is probably due to want of uniformity in working, therefore the following mode of procedure is recommended. After adding milk of lime, evaporate only as far as to leave the mass just moist, then add somewhat more than 50 c.c. of 96 per cent. alcohol, and evaporate the alcoholic extract to 5 c.c.;

extract with absolute alcohol and ether, evaporate the extract until free from alcohol, then dry the residue for at least an hour.

D. A. L.

Estimation of Solid Matter in Wines. By E. Bouilhon (*Compt. rend.*, **103**, 498).—When the total residue in wine is estimated by evaporation in a vacuum, the weight of the residue obtained is lower the greater the surface of the evaporating dish, owing to the loss of part of the glycerol. Three dishes each containing 10 c.c. of wine were placed under the same receiver and kept in a dry vacuum for 8—24 hours. The results are given in grams of solid matter per litre of wine.

	Bordeaux.	Girs.	Rousillon.	Coupage.	Dilute alcohol with 10 p. c. glycerol.
28 sq. c.c. surface..	22·4	30·8	34·2	25·6	34·8
70 „ „ ..	22·0	30·3	33·0	25·1	33·2
70 „ „ .. with sand 5 mm. deep	21·2	29·1	30·4	23·8	31·7

In order to obtain comparable results, flat dishes of the same diameter should be used, and these should contain equal quantities of wine and be placed in the same position in the receiver of the air-pump.

C. H. B.

Estimation of Acidity of Malt. By E. Prior (*Bied. Centr.*, 1886, 647).—The usual way to estimate the acidity of malt is to digest a weighed quantity of ground malt in water for two hours, with frequent agitation, to filter quickly, estimate acidity in an aliquot part, and calculate as lactic acid; the author found that half an hour's digestion with water sufficed to show acidity; he recommends a 20 per cent. dilution by volume of neutral alcohol as the fluid for extraction, the percentage of acidity when this is employed remaining constant for 24 hours.

His method is to dilute ordinary commercial absolute alcohol with four volumes of water, 500 c.c. of this is used to 100 grams of ground malt, digested in the cold for four hours with frequent agitation, filtered, and 100 c.c. titrated with baryta-water.

J. F.

Presence of Nitrites and Nitrates in Milk an Evidence of Adulteration. By M. Schrodt (*Bied. Centr.*, 1886, 629).—Nitrous or nitric acids are not normally found in milk, and when found in a suspected sample should be taken as evidence of dilution, spring water which is often added to dilute it, generally containing either nitrites or nitrates. The objection may possibly be made that the cow's fodder contained nitrates or nitrites; to put this to the proof, the author fed two cows for five days on beets, to which he added 10 grams daily per head of potassium nitrate, notwithstanding which no trace of nitrates, &c., was found in the milk; he therefore thinks the evidence afforded by their presence is conclusive. The method used was that introduced by Soxhlet, the reagent being diphenylamine.

J. F.

Further Notes on the Methods of Examining and Chemistry of Fixed Oils. By A. H. Allen (*J. Soc. Chem. Ind.*, **5**, 65—72, and 282—283).—*Specific Gravity of Oils.*—A convenient instrument for ascertaining the density of fixed oils is Westphal's hydrostatic balance. A counterpoised thermometer suspended from a piece of thin platinum wire is attached to one end of a graduated lever. On immersing the thermometer in a liquid, it loses a certain weight. The equilibrium is restored by hanging on the lever a series of riders, which are adjusted in weight so as to make the reading very simple. As the employment of a thermometer as a plummet renders the instrument unsuited for determinations of density at 100°, or other high temperature, the author substitutes in such cases a plummet of thick glass rod. For the determination of the density of fats the author some time ago recommended the use of a Sprengel tube, and urged that the density should be taken at the boiling point of water. In all cases, however, where there is sufficient substance at disposal, the Sprengel tube has been abandoned in favour of the plummet.

Coefficients of Expansion of Oils.—A series of tables illustrating the rates of expansion of fats and oils are given, showing (1) that the rates of expansion of the fluid fixed oils are not sufficiently different to be of any value for their recognition; (2) that of the fluid fixed oils examined (sperm oil, bottle-nose oil, whale oil, porpoise oil, seal oil, menhaden oil, neats-foot oil, lard oil, olive oil, arachis oil, rape oil, sesamé oil, cotton-seed oil, niger-seed oil, linseed oil, and castor oil) all with the exception of whale oil expand sensibly equally for the same increase of temperature; and (3) that with the exception of whale oil the correction in density for the fluid fixed oils examined may safely be taken at 0·64 for 1° C. (water at 15·5° = 1000).

Viscosity of Oils.—The author is of opinion that Redwood's new form of viscosimeter bids fair to become the recognised standard instrument of the future. For many purposes, however, and especially as a convenient test by oil merchants, the following instrument is likely to grow in favour. It consists of a simple arrangement by which a small paddle-wheel (actuated by a falling weight) is caused to revolve in the sample of oil maintained at a definite temperature by an outer vessel of water. The manipulation is very simple, and the results expressed by the number of seconds required by the weight to fall through a given space are very constant.

Bromine and Iodine Absorptions of Oils.—In order to facilitate the comparison between the results of Mills (*ibid.*, **2**, 435, and **3**, 366) and Hübl (Abstr., 1884, 1435), the author has multiplied the bromine absorptions obtained by Mills by $\frac{127}{80}$, so as to obtain the equivalent iodine absorptions, and has compared the results with the experimental numbers for iodine absorptions obtained by Hübl. The figures which are tabulated in the original paper indicate that the drying oils (containing linoleic acid) assimilate the largest proportions of the haloïds, and their capacity in this respect might probably be employed as a measure of their drying properties. The fish liver oils, however, fully equal the vegetable oils in their assimilating power for haloïds. Hübl's results in the main confirm those of Mills.

Valenta's Acetic Acid Test.—The author has tried this method (Abstr., 1884, 1078) on a number of oils and finds that a slight variation in the strength or proportion of the acid employed is not of importance, and that the temperature at which turbidity occurs with any particular specimen is readily observed and fairly constant. Concordant results have also been obtained from several samples of butter, and it appears probable that further experience may prove the method to afford a simple means of distinguishing butter from butterine.

Determination of Glycerol.—The difficulties attending the determination of the glycerol produced by the saponification of fixed oils have recently been overcome by a method originally suggested by Wanklyn and Fox (Abstr., 1886, 395), and perfected by Benedikt and Zsigmondy. It depends on the saponification of the oil, and oxidation of the glycerol thus formed by potassium permanganate in alkaline solution, with formation of oxalic acid, carbonic anhydride, and water. The excess of permanganate is then destroyed by a sulphite, the solution filtered, the filtrate acidified with acetic acid, and precipitated with a calcium salt. As the precipitate contains calcium sulphate and silicic acid in addition to calcium oxalate, the amount of oxalic acid is determined either by titration of the precipitate with permanganate in acid solution, or by estimating the alkalinity of the ignited precipitate. For the determination of glycerol in fats, the author recommends modifying the method in the following manner :—5 grams of the sample of fixed oil is placed in a six-ounce bottle, together with a solution of 2 grams of caustic potash in 12 c.c. of water. The bottle is securely closed and heated in a water-oven or in boiling water for 8 or 10 hours, the contents being frequently agitated. When the product is perfectly homogeneous and all oily globules have disappeared, the bottle is opened, and the soap diluted with hot water, when a perfectly clear solution should be obtained, except in cases of sperm oil, wax, and other substances yielding insoluble alcohols on saponification. The soap solution is then treated with a moderate excess of acid in the usual way, and the liberated fatty acids are separated from the aqueous liquid containing the glycerol, which latter is then ready for oxidation with alkaline permanganate as above described. D. B.

Maumené's Test for Oils. By C. J. Ellis (*J. Soc. Chem. Ind.*, **5**, 150—152 and 361—362).—The author has made some experiments with the view of extending the application of Maumené's test to drying oils and fish oils, to which it cannot be directly applied without some slight modification, owing to the violent action which ensues when these oils are mixed with concentrated sulphuric acid. To overcome this difficulty it was found necessary to mix with a drying or fish oil some liquid which will moderate the action of the acid on the oil. The author employed a mineral lubricating oil of 0·915 sp. gr. for this purpose, and as on mixing sulphuric acid with such an oil a certain increase of temperature takes place, it is necessary to determine the rise due to each gram of the mineral oil. To accelerate the action of sulphuric acid on the mineral oil, a certain proportion of

colza oil was added, for which the standard number, when not mixed, was accurately determined and found to be 55·8°. Contrary to expectation, it was found that the smaller the quantity of mineral oil in the mixture the greater is the value representing the rise due to each gram of the mineral oil, providing the rise due to each gram of the vegetable oil remains constant whatever the mixture. To calculate the rise in temperature due to each gram of the mineral oil the following formula is employed:—$y = a + bx$, in which y represents the rise in temperature due to each gram of mineral oil, x is the fraction of the mixture consisting of mineral oil, and a and b are constants depending on the conditions of the experiment and the particular mineral oil employed.

In order to obtain the most concordant and trustworthy results, the maximum temperature attained should not exceed 60°, and it is for this reason that the author prefers the use of a mineral oil as the retarding reagent. D. B.

Employment of Congo-red in Titrating Aniline. By P. Julius (*Chem. Ind.*, **9**, 109—110).—Congo-red, the compound of tetrazodiphenyl with naphtholsulphonic acids, is turned blue by acids, and recovers its red colour with an excess of alkali. When used as an indicator in titrating aniline or its homologues with a mineral acid, the point is taken at which a bluish-violet, not changed by small further additions of acid, is produced. A much larger excess is required to produce a pure blue. The results do not vary more than 0·2 per cent. from the theoretical numbers. M. J. S.

Hüfner's Method of Estimating Urea. By E. Pflüger and K. Bohland (*Pflüger's Archiv*, **39**, 1—17).—Pflüger and Schenk previously proved (*ibid.*, **38**, 325) that Hüfner's method of estimating the nitrogen in urine gave results which were too low and variable to found a calculation of the total nitrogen on. Owing to the improvement made in Bunsen's method, the authors have been able to ascertain whether Hüfner's method was sufficiently accurate for the determination of urea only. They find that the results are always too high and also very variable. The variation ranges from 1 per cent. to 10 per cent., and does not therefore admit of compensation. J. P. L.

Estimation of Urea in Human Urine with Sodium Hypobromite. By E. Pflüger and K. Bohland (*Pflüger's Archiv*, **39**, 143—158).—Pflüger's new method of estimating urea by hypobromite (*Pflüger's Archiv*, **38**, 503) can be applied to the estimation of urea in human urine provided the nitrogenous extractives are first removed. For this purpose, a given volume of urine acidified with hydrochloric acid (1 of acid to 10 of urine) is precipitated with sufficient phosphotungstic acid to ensure the separation of all the extractives, the mixture made up to a known volume, and allowed to remain 24 hours at least previous to filtration. The acid filtrate is carefully neutralised with powdered lime, and again filtered through a dry filter.

Great stress is laid on the use of pure soda and bromine for the

preparation of the hypobromite. The mean error of several analyses of urine by this process was + 1·3 per cent. J. P. L.

Qualitative Tests for the Dyes Found in Commerce. By O. N. Witt (*Chem. Ind.*, **9**, 1—7).—A table of reactions for the identification of about 80 artificial colouring matters taken singly. Many commercial dyes are mixtures: in this case, the powder strewn upon wet filter-paper or colourless sulphuric acid will generally give streaks of more than one colour. Where the mixture is more intimate a solution must be made, and the colouring matters withdrawn fractionally by dyeing small pellets of wool or silk in it. The principal adulterant for azo-dyes is sodium sulphate. It is best detected after precipitating the colour by pure sodium chloride. M. J. S.

Detection of Artificially Coloured Red Wine (Claret). By J. Herz (*Chem. Zeit.*, **10**, 968—969; 998).—To 30—50 c.c. of the wine, or if the quantity of colouring matter in the wine is small, 100 c.c. concentrated to 30 c.c., 20—30 c.c. of a saturated solution of magnesium sulphate, and 10—20 c.c. of soda solution are added, stirring well; if necessary the treatment is repeated until the liquid is colourless, or nearly so. The filtrate is made acid with dilute sulphuric acid (1 : 3), and if sulphonic acid colours are present the red colour reappears. The most commonly used member of this group, *acid-magenta* (rosanilinesulphonic acid), yields a violet-red solution, and can be estimated by comparing the tint with magenta solutions of known strength. One mgram. of magenta per litre can be distinctly detected in 30 c.c. of wine without previous concentration. When *archil* (*orseille*) colours are present, the filtrate is bluish, and when made acid turns a litmus-red colour. To test for magenta under such circumstances, Blarez' method of shaking with lead dioxide is used; this destroys the orseille and natural colour. Cazeneuve's method is not recommended. To test for other colours in the magnesium hydroxide precipitate, the gelatinous mass is stirred up with hot water, allowed to settle, and the liquid decanted off. If only the natural colour of the wine is present, or *bilberry* has been used, this liquid is yellow-brown; if *archil* has been used, dark-violet; if *ponceau*, onion or ponceau red; if *cassissine*, pale-red or dark-yellow; if *vinicoline bordelaise*, a yellow-red to yellow-brown liquid, which when poured on sulphuric acid gives a violet ring. By shaking the coloured liquid with amyl alcohol, *ponceau* yields an onion-red residue; *vinicoline*, a dark-brown one; *cassissine*, a dirty-green, violet at the edge, turned yellow by strong hydrochloric acid. The precipitate is a dark-grey or brownish-grey colour when the natural or vegetable colours only are present; with *archil*, it is violet; with *magenta* (acid or ordinary), dirty white; with *cassissine*, dirty yellow-brown; with *vinicoline*, crimson-red. The precipitate is mixed with sand, dried, and extracted with ether; the extract contains any ordinary magenta which can be identified in the usual manner by dyeing wool, or *cassissine* which dyes wool red-brown and leaves a yellow-brown residue in the dish. The dyed wool becomes yellow when treated with strong hydrochloric acid and colourless with ammonia. When

wine is shaken with amyl alcohol, and the coloured extract evaporated, the residue, if it contains the substances named, behaves in the manner described below :—

		With concentrated		
		H_2SO_4.	HCl.	NaHO.
Archil	violet-red	blue	red	blue
Bordeaux, B....	carmine	carmine	carmine	carmine
Ponceau, RRR..	dark-red	crimson	crimson	brown
Cassissine.....	violet-purple	yellow	yellow-brown	red
Vinicoline Bordelaise	cherry-red	brown	red	brown

whilst the wine after extraction is cherry-red with ordinary *magenta*, violet-red with *acid-magenta*, dark-cherry with *Bordeaux*, yellow-red with *ponceau*. Wine coloured with *magenta* produces a violet froth. The detection of vegetable colouring matters in presence of the natural colour of wine or otherwise is a matter of great difficulty, and most of the known methods are ineffectual; it is, however, effected by the author with comparative facility in the following manner:—10 to 15 c.c. of wine is shaken with 5 c.c. of a saturated solution of tartar emetic, and then examined by reflected and transmitted light either at once or, if no immediate change has taken place, after some time. This treatment produces with genuine red wine always a cherry-red colour, and with other substances as follows:—*Red-poppy* (*Papaver rhœus*), dark cherry-red; *cherry*, violet; commercial *elder* colouring matter, red-violet; *bilberry* (*Vaccin. myrtill*), blue-violet; *privet-berry*, pure violet. White wines artificially coloured, and red wines mixed with artificial colours have been successfully examined in this manner; in the latter case the wine some time after treatment is compared with a genuine red wine to distinguish more readily the change of colour. Old solutions of privet do not give the colour change. Sodium hydrogen carbonate produces with pure wine, brown-red; with wine coloured with pure *elderberry*, grey-violet; and with *bilberry*, brown-green. Tartar emetic appears to form an antimony lake with the colouring matters. With practice, all the above-mentioned colours can be detected in 30—50 c.c. of wine. In the subsequent communication (*loc. cit.*, 998), the author acknowledges the priority of Ambühl and Elsner's recommendation of the use of tartar emetic for the purpose in question. They, however, recommend hot solutions; the author finds cold better. Fermented bilberries give the violet colour even better than unfermented berries, especially when fresh, inasmuch as oxidation interferes with the delicacy after a time. The distinctness of this colour is increased by diluting the wine. D. A. L.

General and Physical Chemistry.

Chemical Changes produced by Sunlight. By E. Duclaux (*Compt. rend.*, **103**, 881—882).—Many organic compounds are affected by solar radiation in the same way as by microbes, the products of the change being water and carbonic anhydride, with other substances which are relatively stable in the conditions under which they are produced, and are identical with the products of the action of microbes.

Cane-sugar in neutral or alkaline solution is not affected by prolonged exposure to sunlight, but if slightly acidified even with an organic acid it is readily inverted by solar radiation. The solution of invert sugar undergoes no further change so long as it remains acid, but if made alkaline the glucose is rapidly decomposed with formation of water, carbonic anhydride, oxalic, formic, and acetic acids, and about 3 per cent. of alcohol. A similar change takes place, although less rapidly, out of contact with the air, and hence it is evident that the decomposition is due to internal combustion.

Lactose and lactates also yield alcohol under similar conditions. The exact nature of the change in any case is modified by the nature of the source from which oxygen is absorbed (air, salts of platinum, gold, mercury); but the chief products are practically the same from all substances. These products are alcohol, oxalic acid, acids of the acetic series, leucine, carbamide, carbonic anhydride, water, &c. Certain differences are, however, observed. Tartaric acid gives aldehyde in place of alcohol, and the alcohols, if oxidation is regular, tend to produce the corresponding acid of the acetic series. C. H. B.

Practical Methods of Photographing the Spectrum. By J. M. Eder (*Monatsh. Chem.*, **7**, 429—454).—This paper contains a description of some practical methods of photographing the various parts of the spectrum by silver bromide gelatin plates sensitised by different dyes. The preparation of the plates and the processes used for the development are described in full, and accompanied by copies of photographs taken.

For spectra from the ultra-violet to the yellow, about D, the best dyes are erythrosin, benzopurpurin 4B, and quinoline-red; from the ultra-violet to the red cyanin, is the best; from the orange to the red, cœrulein with red glass, and "sensitive green," a dye from para-hydroxybenzaldehyde and dimethylaniline, are recommended. These plates, sensitive to the green, yellow, or red part of the spectrum, are suitable for photography by petroleum and gas light, and for taking photographs of gilded documents and papyri, of microscopic preparations, and of clouds on a blue sky, interposing yellow glass to subdue the blue. Excellent photographs of stars have been taken with the aid of these plates. V. H. V.

Electrolysis of Carbon Compounds. By J. Habermann (*Monatsh. Chem.*, **7**, 529—551).—In continuation of former experiments on the electrolysis of carbon compounds (Abstr., 1881, 215), the author describes the results which are obtained under various conditions with alcohol acidified with sulphuric acid, or rendered alkaline by soda, and with potassium acetate dissolved in methyl alcohol or its homologues. The sources of electrical energy used were a thermo-battery of 120 elements, a Smee's battery of 16 elements, and a dynamo-machine of one horse-power.

On electrolysis, alcohol acidified with sulphuric acid yields hydrogen evolved as gas at the negative pole, aldehyde, and after prolonged action aldehyde-resin together with ethyl hydrogen sulphate. The main reaction is therefore $C_2H_6O = C_2H_4O + H_2$. If the alcohol is rendered alkaline, or is in the form of sodium ethoxide, the products of decomposition are hydrogen, carbonic anhydride as sodium carbonate, an aldehyde-resin insoluble in ether and alcohol, together with a soluble modification, and a substance allied to cinnamaldehyde.

A concentrated solution of potassium acetate in ethyl alcohol yields a mixture of hydrogen and ethane together with potassium ethyl carbonate, by the mutual decomposition of the salt and acid. In fact, the process serves as a convenient method for the preparation of potassium ethyl carbonate in large quantities, as the salt separates in fine crystalline aggregates. It is quickly decomposed by water, but dissolves in absolute alcohol without change.

The results obtained with solutions of potassium acetate in methyl and butyl alcohols were unsatisfactory. V. H. V.

Phosphates. By Berthelot (*Compt. rend.*, **103**, 911—917).—When ammonium chloride is added to a solution of trisodium phosphate there is an absorption of heat which varies with the proportion of ammonium chloride, being 5·96, 5·63, 4·84, and 2·62 cal. for 3, 2, 1 and $\frac{1}{2}$ mols. of ammonium chloride respectively. Complete decomposition of the sodium phosphate would correspond with an absorption of heat equal to −6·4 cal., and hence it is evident that the action of the ammonium chloride is almost complete, although the water exerts a greater dissociating effect on the ammonium phosphate than on the sodium salt.

If trisodium phosphate is added to a solution of a magnesium, barium, strontium, calcium, or manganese salt, a colloïdal precipitate of the insoluble phosphate is at first formed, and there is considerable absorption of heat, but after some minutes the precipitate becomes crystalline and a large quantity of heat is developed. The heats of formation of the colloïdal and crystallised phosphates are given in the following table:—

	Colloïdal.	Crystallised.
Magnesium phosphate	57·8 cal.	83·0 cal.
Magnesium hydrogen phosphate	50·6 ,,	54·2 ,,
Barium phosphate	68·4 ,,	100 8 ,,
Strontium phosphate	65·4 ,,	97·4 ,,
Calcium phosphate	64·0 ,,	— ,,
Manganese phosphate	45·8 ,,	52·5 ,,

In the case of barium phosphate, the sodium phosphate must be added to the barium chloride, and not *vice versâ*, otherwise the change to the crystalline state is too rapid. The phenomena now described explain the discordant results obtained by Louguinine and the author for the heat of neutralisation of phosphoric acid by baryta, and also the differences observed by Blarez (this vol., p. 7) between the heats of formation of barium phosphate and barium arsenate. In the case of strontium also, the change to the crystalline condition is extremely rapid, if the strontium solution is poured into that of the trisodium phosphate. Calcium phosphate was obtained only in the colloïdal form.

The heats of formation of the colloïdal insoluble phosphates do not differ to any great extent from the heat of formation of an equivalent quantity of trisodium phosphate, 33·6 × 2 cal. In other words, the precipitate in its initial condition corresponds closely with the soluble salt from which it has been derived, a further example of the tendency of systems which are undergoing transformation to preserve their molecular type. On the other hand, the new phosphates may be dissociated by water to a greater extent than the soluble phosphate from which they have been formed; and this dissociation will be accompanied by an absorption of heat. This absorption is practically *nil* with barium phosphate, which approximates closely to the alkaline phosphates, but it is very distinct with magnesium phosphate, which is more readily dissociated.

In dissolved trisodium phosphate, the third and even the second equivalents of the base are less intimately combined with the acid than the first atom, and are partially separated from it by the dissociating action of the solvent. There can be little doubt that this imperfect state of combination also exists in the colloïdal insoluble phosphates, the formation of which is due to a polyalcoholic rather than an acid function of the phosphoric acid. The combination, however, soon becomes more intimate, and the alcoholic function changes to an acidic function comparable with that of ordinary tribasic acids, the change being accompanied by development of heat and crystallisation of the phosphates. The actual development of heat is much greater than can be supposed to be due to the mere physical change from the colloïdal to the crystalline condition, even if the change were accompanied by combination with water. As a matter of fact, the crystallised phosphate contains less water than the colloïdal phosphate. In their new condition, the heats of formation of the insoluble phosphates become practically treble that of the ordinary monophosphates, or in other words, the three acid functions become equivalent to one another, and to this change is due the greater proportion of the heat developed in the passage from the colloïdal to the crystalline form.

C. H. B.

Heats of Neutralisation of Homologous and Isomeric Acids. By H. Gal and E. Werner (*Compt. rend.*, **103**, 806—809).—The author has determined the heats of neutralisation of isobutyric, isopropylacetic, trimethylacetic (pivalic), caproic, isobutylacetic, and sorbic acids, and his results, together with the heats of neutralisation of the lower acids of the acetic series, as determined by Berthelot,

Louguinine, and others, are given in the following table. Heat of solution of isobutyric acid, directly + 0·973 cal., indirectly + 1·012 cal.; isopropylacetic acid, directly + 1·167, indirectly + 1·030.

Acid.	Heat of neutralisation.
Formic acid, H·COOH	13·3
Acetic acid, Me·COOH	13·4
Propionic acid, $CH_2Me·COOH$	14·3
Normal butyric acid, $CH_2Me·CH_2·COOH$	14·4
Isobutyric acid, $CHMe_2·COOH$	13·9
Normal valeric acid, $CH_2Me·CH_2·CH_2·COOH$	14·4
Isopropylacetic acid, $CHMe_2·CH_2·COOH$	14·4
Trimethylacetic acid, $CMe_3·COOH$	13·674
Normal caproic acid, $CH_2Me·CH_2·CH_2·CH_2·COOH$	14·689
Isobutylacetic acid, $CHMe_2·CH_2·COOH$	14·5

Omitting formic and acetic acids, the heat of neutralisation of the other acids, with the exception of isobutyric and trimethylacetic acids, is practically constant, and varies between 14·3 and 14·6. Isobutyric acid is a secondary acid, and trimethylacetic acid is a tertiary acid, and it would seem therefore that the heat of neutralisation of primary acids is greater than that of secondary acids, whilst that of tertiary acids is somewhat smaller still. The heat of neutralisation of sorbic acid, which is regarded by Menschutkin as a tertiary acid, is 12·945.

C. H. B.

Heats of Neutralisation of Malonic, Tartronic, and Malic Acids. By H. Gal and E. Werner (*Compt. rend.*, **103**, 871—873).—*Malonic Acid.*—Heat of solution at 10° = −4·573 cal. Heat of neutralisation by soda: 1st equivalent, 13·342 cal.; 2nd equivalent, 13·778 cal.; total, 27·120 cal.

Tartronic Acid.—Heat of solution at 12° = −4·331 cal. Heat of neutralisation by soda: 1st equivalent, 13·711 cal.; 2nd equivalent, 11·856 cal.; 3rd equivalent, 0·0 cal.; total, 25·567.

Malic Acid.—Heat of solution at 20° = −3·148 cal. Heat of neutralisation by soda: 1st equivalent, 12·730 cal.; 2nd equivalent, 12·189 cal.; 3rd equivalent, 0·0 cal.; total, 24·919.

The heat of neutralisation of oxalic acid is 28·1 cal. (Berthelot and Thomsen); of succinic acid, 26·4 cal. (Chroutschoff); and tartaric acid, 25·3 cal. (Berthelot).

It is evident from these values that the heat of neutralisation diminishes as the molecular weight increases. The introduction of the OH group into oxalic, malonic, and succinic acids lowers the heat of neutralisation by about 2 cal. A similar difference has previously been observed between propionic and lactic acids, and between benzoic and the hydroxybenzoic acids. C. H. B.

Thermochemistry of Reactions between Magnesium Salts and Ammonia. By Berthelot (*Compt. rend.*, **103**, 844—848).—When magnesium sulphate solution is mixed with an equivalent quantity of sodium hydroxide solution, there is an immediate develop-

ment of +0·18 cal., but the development of heat gradually slackens, and at the end of 10 minutes is + 1·14 cal. The successive developments of heat are due to the fact that a basic salt is first formed, which is afterwards decomposed by the soda, and also to the hydration, contraction, &c., of the precipitate. Magnesium chloride and sodium hydroxide behave in like manner. At first there is an absorption of −0·32 cal., and afterwards a development of +0·32 cal., the final result being *nil*.

It is evident, as the researches of Thomsen, Favre and Silbermann, Ditte, and others have already indicated, that the heat developed by the action of acids on magnesium hydroxide approximates closely to that developed by their action on potash and soda.

The action of ammonia on magnesium sulphate is accompanied by an absorption of −0·24 cal., whereas if the magnesium were completely displaced, 3·0 cal. should be absorbed. The difference is due to the formation of double salts or oxides, the production of which is accompanied by a development of +2·8 cal. With magnesium chloride, the difference between the calculated and observed values is +2·2 cal.

If magnesium sulphate is mixed with 2 mols. of ammonium chloride, +0·32 cal. is developed, and if an equivalent quantity of ammonia is now added, there is a further development of +0·26 cal., the total development of +0·58 cal. being due to the formation of a complex oxide, the heat of neutralisation of which is 0·58 cal. higher than the sum of the heats of neutralisation of magnesium oxide and ammonia separately. When magnesium chloride is mixed with ammonia, there is an absorption of −0·48 cal., and if ammonium chloride is then added there is a development of +0·56 cal., the sum being 0·08 cal., from which it follows that the heat of neutralisation of the complex oxide by hydrochloric acid is practically identical with that of magnesium oxide.

If magnesium sulphate or chloride solution is mixed with sodium hydroxide, and ammonia then added, the greater part of the precipitate redissolves, but there is no sensible thermal disturbance, a result which indicates that the heat of solution of the precipitate is identical with its heat of combination with the solvent. If, on the other hand, magnesium sulphate is first mixed with ammonia, and the sodium hydroxide added afterwards, there is a development of +1·90 cal., probably due to the fact that, the order of admixture being reversed, the liquid requires a much longer time to attain the same condition. The difference between the observed thermal disturbance and the development of heat resulting from the action of soda or magnesium sulphate alone is a further proof of the formation of complex compounds.

If magnesium sulphate is mixed with 2 mols. of ammonium chloride and sodium hydroxide then added, +3·64 cal. are developed, and some permanent precipitate is formed. The thermal disturbance is greater than that which would correspond with the displacement of ammonium by sodium, and the difference indicates the combination of magnesia and ammonia with formation of ammonio-magnesium sulphate. If 4 mols. of ammonium chloride are added at the begin-

ning, no precipitate is formed, and the heat developed is +3·90 cal. With magnesium sulphate, the excess of heat developed above that corresponding with the decomposition of the ammonium salt is +1·2 cal., with the chloride it is +1·0 cal.

From these results it follows that the complex ammonio-magnesium bases in uniting with sulphuric or hydrochloric acid, develop about +1·8 cal. more than pure ammonia, and +0·3 cal. more than magnesium oxide. The association of ammonia with a metallic oxide such as magnesia would seem to result in the production of a complex alkali analogous to tetramethylammonium oxide, with an energy greater than that of metallic oxides, and approaching that of the strongest alkalis. C. H. B.

Heats of Combustion and Formation of Homologous Phenols. By F. Stohmann, P. Rodatz, and H. Herzberg (*J. pr. Chem.* [2], **34**, 311—327).—In this paper a series of determinations of the heats of combustion and formation of the homologous series of phenols are given in detail, as also their heats of liquefaction. The principal values obtained are given in the following table:—

	Heat of combustion per gram-molecule.	Heat of formation.
Phenol (solid), $C_6H_5{\cdot}OH$	723659	—
„ (liquid)	726002	—
Orthocresol (liquid), $C_6H_4Me{\cdot}OH$	883008	50992
„ (solid)	879788	—
Metacresol (liquid)	880956	53044
Paracresol „	882900	51100
„ (solid)	880441	—
Orcinol, $C_6H_3Me(OH)_2$ (solid)	824724	109276
Orthoxylenol, $C_6H_3Me_2{\cdot}OH$ (solid)	1035434	61566
Metaxylenol (liquid)	1037499	59501
Paraxylenol (solid)	1035638	61362
Pseudocumenol, $C_6H_2Me_3{\cdot}OH$ (solid)	1191451	68549
Carvacrol, $C_6H_3MePr{\cdot}OH$ (liquid)	1354819	68181
Thymol (liquid)	1353750	69250
„ (solid)	1349982	—

On a comparison of these numbers, it will be seen that every displacement of hydrogen by a methyl-group corresponds with an increment of 156356 cal. in the heat of combustion, a value practically equal to that obtained for the homologues of methyl alcohol. Thus it follows that the displacement of hydrogen by methyl, either in the so-called side-chain or in the nucleus, corresponds with the same value for the heat-increment. Thus the value for ethylphenol will be equal to that of xylenol. Similarly also, as the values for carvacrol and thymol are approximately equal to that of pseudocumenol, namely, the introduction of the isopropyl-group produces the same effect as that of three single methyl-groups, then the heat values of the iso- are equal to those of normal-compounds. V. H. V.

Some Laws of Chemical Combination. By DE LANDERO and R. PRIETO (*Compt. rend.*, **103**, 934—935).—If chemical combination is taken as the clashing together of the particles of the elements, and if each particle is regarded as possessing a constant velocity which is characteristic of the particular element, the loss of energy resulting from the union of the non-elastic particles may be regarded as the equivalent of the quantity of heat developed by the combination. These considerations lead to the formula—

$$f = \frac{ee'}{2(e + e')} (\mathrm{V} + \mathrm{V}')^2,$$

in which f = the heat of combination expressed in calories, e, e' = the weights of the combining elements *equivalent* to 1 gram of hydrogen, whilst V and V′ are quantities which are constant for each element and are proportional to the velocities of their particles. These quantities may be termed *thermodynamic constants*, or *thermodynamic equivalents*, and their value is obtained by the formula—

$$\mathrm{V} \pm \mathrm{V}' = \sqrt{2f \frac{e + e'}{ee'}}.$$

Take the case of the two copper bromides—

Cuprous bromide: $e + e' = 143{\cdot}4$; $f = 25900$ cal.; $\mathrm{V} + \mathrm{V}' = \pm 38{\cdot}269$

Cupric bromide: $e + e' = 111{\cdot}7$; $f = 17300$ cal; $\mathrm{V} \pm \mathrm{V}' = \pm 39{\cdot}039$.

Calculations with tin bromides, mercury bromides, mercury iodides, &c., lead to similar results. Since V ± V′ is the sum or difference of the thermodynamical equivalents of the two elements in each system; it is necessary to obtain the constants of some of the elements from different sets of compounds, care being taken to use only thermochemical data referred to the solid state. The following table gives the thermodynamical equivalents of several elements, these values referring in each case to that quantity of the element which is equivalent to 1 gram of hydrogen:—

K	45·221	S	47·874	Al	48·218
Na.....	49·768	Tl.....	5·223	Zn.....	13·073
Hg.....	9·079	Ag	12·786	Pb.....	5·155
Br.....	44·171	Cu	4·999	Si	37·519
I	32·416	Ca	50·309		

C. H. B.

The Law of Volumes in Chemistry. By T. S. HUNT (*Chem. News*, **54**, 206—207).—The author advocates the universal application of the law of volumes to solids, liquids, and gases, which would render the application of the atomic hypothesis to explain the law of definite proportions wholly unnecessary. From this standpoint, the union of many volumes of vapour or gas to form a single volume of vapour or solid would be regarded as chemical combination; the reverse, namely vaporisation, would be chemical decomposition, which would be without specific difference in the case of integral volatilisation, or

with definite changes, as in cases now regarded as dissociation. The difference between chemical and physical molecules would hence be quite evident. D. A. L.

Velocity of Dissociation. By H. Lescœur (*Compt. rend.*, **103**, 931—933).—The velocity of dissociation of acid sodium acetate, $C_2H_3O_2Na,2C_2H_4O_2$, was determined by placing the compound in a small bell-jar which also contained soda-lime; the temperature of the whole being kept at 100°. The mean velocity of dissociation during a given interval is determined by dividing the time into the loss of weight of the compound. The results indicate the existence of a biacetate, $C_2H_3O_2Na,C_2H_4O_2$, and a sesquiacetate, $2C_2H_3O_2Na + C_2H_4O_2$.

Velocity of dissociation does not depend on the temperature alone, as Müller-Erzbach supposes, but also on the physical condition of the substance which is undergoing dissociation. In this particular case, the rate of dissociation increased fourfold when the acetate became solid, although the tension of dissociation did not change, and similar phenomena are observed with copper sulphate crystals, &c.

C. H. B.

Nature of Liquids. By W. Ramsay and S. Young (*Chem. News*, **54**, 203—205).—It is proved by various investigations that, above a certain pressure and temperature, all liquids show an increase in the density of their saturated vapours beyond that deducible from the molecular formulæ, varying of course with the liquid. Some liquids, however, known to be dissociable, in addition show an increase also on fall of temperature and pressure below a certain temperature and pressure characteristic of the liquid. Reasoning from these facts, the following difference is suggested between stable and dissociable liquids:—In the former, the molecules exhibit physical but not chemical attraction; in the latter both physical and chemical attraction are evident, inasmuch as, besides cohesion and surface tension, there is evidence of molecular combination. The behaviour of vapours at the moment the liquid is visible support this theory, for whereas vapours from dissociable liquids continue to rise in pressure in spite of the decrease in volume and condensation of liquid (evidence of non-homogeneity of the vapour, owing in these instances to formation of molecules of higher molecular weight), vapours from stable liquids do not behave in this manner, but the pressure in such case is the vapour-pressure corresponding with the temperature; hence it may be concluded that the latter show no tendency to form complex molecular groups.

With regard to the solvent action of a fluid above its critical point, the authors have worked with a solution of eosin in alcohol, taking the fluorescence as indicating solution. They find that solution existed at least for a short time at temperatures a little above the critical point, and at volumes smaller than the critical volume; apparently, however, after some time the solid is wholly deposited as such on the walls of the tube. This is not conclusive, as the translucent red substance deposited on the glass interfered with the detection of the fluorescence. According to the authors' view of the nature of liquids,

solution should be possible above the critical point provided the volume is sufficiently small. D. A. L.

Capillary Constants and Meniscus Angle. By J. Traube (*J. pr. Chem.* [2], **34**, 292—311).—Determinations are given for the value of the function $\alpha^2 \cos\theta$ according to the formula $rh = \alpha^2 \cos\theta$, for aqueous solutions of the alcohols of the paraffinoïd series and acids of the acetic series at various degrees of concentration (comp. Abstr., 1885, 1033). The principal points to be noticed are that both propyl and isopropyl alcohols show a minimum value for the function with mixtures of equal weights of the alcohol with water, and that the curve for butyric acid at first decreases with increase of concentration up to 30 per cent., thence increases up to 50 per cent., and subsequently decreases.

After a historical review of the literature on the magnitude of drops, an account is given of experiments, made with an apparatus previously described, permitting of the formation of drops from a capillary tube under constant or variable conditions of temperature and pressure. The weight of the drops was ascertained by determinations of the specific gravity and the number of drops in a constant volume. The results obtained with the above-mentioned alcohols and acids show that the *volume of the drops is proportional to the rise in height in the capillary tube, or their weight is proportional to the product of the height and the specific gravity*. If then the mean weight of the drop is divided by the circumference $\frac{C}{2\pi r}$, then for all liquids examined this quotient is less than the capillary constant $\alpha \cos\theta$, and secondly this quotient increases with decrease of radius of the tube. Both these statements are deducible from the previous observations of Hagen and Quincke.

Again the diameter of the capillary tube determines the shape of the drop; thus with tubes of less than 3—4 mm. their form is more or less spheroidal, with tubes of 1 mm. the form is cylindrical with a convex base, and with tubes of larger diameter it is paraboidal. V. H. V.

Crystallisation by Diffusion. By C. E. Guignet (*Compt. rend.*, **103**, 873—875).—The experiments described in this paper are an extension of Becquerel's researches on electro-capillary reactions.

The introduction of any solid into a saturated solution of another solid determines the crystallisation of the latter, provided that the solid introduced is soluble in the particular solvent. For example, solid paraffin introduced into a saturated solution of sulphur in carbon bisulphide causes the separation of crystals of sulphur, and *vice versâ*; sodium thiosulphate introduced into a saturated solution of ammonio-cupric sulphate yields violet needles of ammonio-cupric thiosulphate.

If crystals of sodium sulphate are placed in a saturated solution of barium chloride, the crystals become opaque but retain their form, and when the crystals are broken each one is found to be a sort of

miniature lode with crystals of barium sulphate. Barium chloride introduced into a saturated solution of sodium sulphate yields only amorphous barium sulphate, probably because the chloride dissolves too quickly. Ordinary sodium phosphate placed in magnesium sulphate solution produces crystallised magnesium phosphate.

In order to observe these phenomena with two liquids, if the action is merely physical, a saturated solution of a solid is covered with a layer of the solvent, and on this is poured a second liquid in which the solid is somewhat less soluble than in the first. The liquids gradually mix by diffusion, and the solid separates in very distinct crystals. If a saturated solution of sulphur in carbon bisulphide is covered with a layer of the bisulphide, and on this is poured a layer of oil, alcohol, glacial acetic acid, benzene, petroleum, &c., octahedral crystals of sulphur are deposited. A saturated solution of lead chloride in hydrochloric acid covered in a similar manner with a layer of hydrochloric acid and a layer of water, yields fine crystals of lead chloride.

Where chemical action takes place between the liquids, one is placed in a crystallising dish which is filled nearly to the top, and this is placed inside another vessel which contains the second liquid. Water is then carefully poured into both dishes until it is just higher than the edge of the inner dish. Diffusion takes place through the supernatant water, and crystals are formed. Sodium sulphate and calcium chloride give long crystals of calcium sulphate; sodium sulphate and barium chloride give crystallised barium sulphate; sodium sulphate and lead acetate give crystals of lead sulphate; and potassium ferrocyanide and lead acetate yield long pale-yellow needles of lead ferrocyanide.

On a large scale, wooden vessels with a leaden partition which does not quite reach to the top are used. The liquids are poured one into each compartment, and the latter are then filled up with water until the water just flows over the top of the partition. In this way very large crystals can be obtained. C. H. B.

Influence of some Normal Salts on the Decomposition of Methyl Acetate by Hydrochloric and Sulphuric Acids. By H. Trey (*J. pr. Chem.* [2], **34**, 353—377).—Ostwald investigated (*J. pr. Chem.* [2], **23**, 209) the difference in the action of acids caused by the presence of their normal salts; the author has repeated these experiments with a view to obtaining a satisfactory explanation of this action. The experiments were made with hydrochloric and sulphuric acids, and the salts of these acids with the alkalis and alkaline earths. The methyl acetate method was used, in the manner previously described, with normal acids (1 gram-equivalent in 1 litre) and normal acids to which $\frac{1}{4}$, $\frac{1}{2}$, 1, &c., equivalents of their normal salts had been added. These normal solutions were also used $2\frac{1}{2}$, 5, and $12\frac{1}{2}$ times diluted. The results were calculated according to the formulæ given by Ostwald (this Journal, 1884, 581), and are given in a series of tables. These values are not strictly comparable, but require correcting for the increase of volume caused by the addition of salt and the consequent decrease of the velocity of the reaction. The

mean values found are given below; the second line in each case gives the corrected value.

Hydrochloric Acid and Alkaline Chlorides.

	HCl (1 litre).	HCl (1 litre) + ¼NaCl.	HCl (1 litre) + 1NaCl	HCl (1 litre) + 4NaCl.	HCl (1 litre) + ¼KCl.	HCl (1 litre) + 1KCl.	HCl (1 litre) + 3KCl.
Normal.....	31·27	32·76	36·87	52·87	31·89	34·66	40·83
	—	32·87	37·49	57·62	32·16	35·05	44·60
$\frac{1}{2\frac{1}{2}}$ normal ..	11·69	11·75	12·27	13·88	11·73	11·89	12·45
	—	11·82	12·35	14·88	11·83	12·26	13·64
$\frac{1}{5}$ normal....	5·62	5·61	5·75	6·09	5·63	5·63	5·60
	—	5·68	5·85	6·64	5·67	5·80	6·14
$\frac{1}{12\frac{1}{2}}$ normal..	2·22	2·23	2·20	2·15	2·21	2·15	2·10
	—	2·24	2·24	2·34	2·22	2·22	2·30

Calculating the ratio in which the velocity of action of the hydrochloric acid is increased by the addition of the above salts, the following numbers are obtained:—

	HCl (1 litre).	HCl (1 litre) + ¼NaCl.	HCl (1 litre) + 1NaCl.	HCl (1 litre) + 4NaCl.	HCl (1 litre) + ¼KCl	HCl (1 litre) + 1KCl.	HCl (1 litre) + 3KCl.
Normal	1·000	1·051	1·199	1·843	1·028	1·121	1·426
$\frac{1}{2\frac{1}{2}}$ normal ..	1·000	1·011	1·056	1·273	1·012	1·049	1·167
$\frac{1}{5}$ normal....	1·000	1·011	1·041	1·181	1·009	1·032	1·005
$\frac{1}{12\frac{1}{2}}$ normal..	1·000	1·009	1·009	1·054	1·000	1·000	1·093

For the stronger solutions, the increase of the action of the hydrochloric acid is proportional to the amount of salt present; for the weaker solutions, the increase is so small as to fall within the errors of experiment.

Hydrochloric acid and lithium, magnesium, calcium, strontium, and barium chlorides, gave the following numbers:—

	HCl (1 litre).	HCl (1 litre) + 4LiCl.	HCl (1 litre) + 2$MgCl_2$.	HCl (1 litre) + 2CaCl.	HCl (1 litre) + 2$SrCl_2$.	HCl (1 litre) + 1$BaCl_2$.
Normal	31·27	56·83	66·56	59·43	58·55	42·46
	—	61·31	69·26	62·69	62·06	44·07
$\frac{1}{5}$ normal....	5·62	5·97	6·33	6·24	6·20	5·84
	—	6·44	6·59	6·56	6·58	6·07

These numbers gave the following ratios for the accelerating action of the salts:—

	HCl (1 litre)	HCl (1 litre) + 4LiCl.	HCl (1 litre) + 2$MgCl_2$.	HCl (1 litre) + 2CaCl.	HCl (1 litre) + 2$SrCl_2$.	HCl (1 litre) + 1$BaCl_2$.
Normal.....	1·000	1·961	2·215	2·005	1·985	1·409
$\frac{1}{5}$ normal....	1·000	1·146	1·173	1·167	1·171	1·080

From these results the author concludes that the accelerative influence of the chlorides stands in the inversive ratio to the atomic weights of the respective series. Thus, calculated for 1 equivalent of chloride, the numbers are:—

LiCl.	NaCl.	KCl.	$MgCl_2$.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.
1·240	1·199	1·121	1·304	1·251	1·246	1·205

These results agree with those found by Reicher (Abstr., 1885, 1034) for the saponification of ethyl acetate by alkalis.

The action of sulphuric acid in the presence of normal sulphates is the reverse of that of hydrochloric acid. The action is retarded nearly proportionally with $\frac{1}{4}$ to 1 equivalent salt, but in a less degree with 2 equivalents. The following tables give the mean values for normal and $\frac{1}{5}$ normal solutions:—

	$\frac{1}{2}H_2SO_4$ (1 litre).	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{8}Na_2SO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{4}Na_2SO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + 1Na_2SO_4.
Normal .	{ 16·62 —	14·71 14·71	12·58 12·64	9·50 9·62	6·89 7·08
$\frac{1}{5}$ normal	{ 3·34 —	3·04 3·04	2·68 2·69	2·16 2·19	1·62 1·67
Normal .	1·000	0·885	0·760	0·578	0·426
$\frac{1}{5}$ normal	1·000	0·910	0·805	0·656	0·500

With sulphuric acid, the retarding influence of the sulphates on the velocity of the action appears to *increase* with the atomic weight of the elements of the series, thus :—

$\frac{1}{2}H_2SO_4$ (1 litre).	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{2}MgSO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{2}Li_2SO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}H_2SO_4$ (1 litre) + $\frac{1}{2}K_2SO_4$.
1·000	0·787	0·620	0·579	0·530

Dithionic acid in the presence of its normal salts was influenced in the same way as hydrochloric acid, so also was the bibasic methylenedisulphonic acid, whilst dichloracetic acid behaved like sulphuric acid. This method of investigation will therefore throw no light on the basicity of dithionic acid, but the author thinks the results show that it does not form acid salts in aqueous solution.

G. H. M.

Preservation of Gases over Mercury. By H. B. Dixon (*Chem. News*, **54**, 227—228).—From the author's experiments, it is shown that, provided due precautions are taken to prevent the formation of a film between the glass and the mercury, gases may be safely preserved over mercury for a considerable time. D. A. L.

Cracking Glass with Certainty. By E. Beckmann (*Zeit. anal. Chem.*, **25**, 530—531).—A scratch is made with a file; at both sides of this, pads of wetted filter-paper are wrapped round the object, leaving a space of a few millimetres between them. The flame of a Bunsen or gas blowpipe is applied to this space, when the crack will be carried round from the scratch midway between the two pads.

M. J. S.

Apparatus for Chemical Laboratories. By J. Walter (*J. pr. Chem.* [2], **34**, 427—432).—A new form of condenser, and flasks for use with it, both for ordinary and fractional distillation.

G. H. M.

Inorganic Chemistry.

Action of Hypochlorous Anhydride on Iodine Trichloride. By H. Bassett and E. Fielding (*Chem. News*, **54**, 205—206).— Iodic anhydride is the main product of the reaction when solutions of iodine trichloride and hypochlorous anhydride in carbon tetrachloride are mixed, or when a current of hypochlorous anhydride is passed through a solution of iodine trichloride, or even over solid trichloride. In the last case, the action is very slow. D. A. L.

Saturation of Selenious Acid by Bases. By C. Blarez (*Compt. rend.*, **103**, 804—806).—With cochineal or helianthin (methyl-orange), selenious acid is monobasic. With litmus, it is monobasic to ammonia, lime, strontia, and baryta, but if soda or potash is used the litmus only becomes blue-violet when about 1·5 equivalent of alkali is added. With phenolphthaleïn and potash, soda, ammonia, lime or strontia, the colour change takes place when somewhat more than 1·5 equivalent of alkali is added, but with phenolphthaleïn and baryta selenious acid is bibasic, and the colour change is sharp and distinct.

Selenious acid can be accurately titrated by means of standard baryta solution, using helianthin or phenolphthaleïn as indicator. The baryta has double the value with the first indicator that it has with the second. Both indicators can be used in the same solution; the rose colour of the helianthin disappears when the acid is half saturated, and the rose colour due to the change of the phenolphthaleïn becomes visible when saturation is complete.

As no basic barium selenite is formed when baryta is present in excess, an excess of baryta can be determined by means of phenolphthaleïn and a standard acid in the liquid containing the precipitated barium selenite.

Selenious acid, like sulphurous acid, can be estimated in presence of other acids by means of baryta, provided that the total basicity of these acids is indicated by helianthin. Helianthin and phenolphthaleïn are both added to the same solution, and the amount of selenious acid is calculated from the quantity of baryta solution required to produce the second colour change, this quantity being exactly half that which would be required to neutralise the selenious acid alone with phenolphthaleïn as the indicator. C. H. B.

Formation of Nitrites. By S. Kappel. (*Arch. Pharm.*, [3], **24**, 897—900).—The author has extended his observations made on the action of copper, iron, and zinc in contact with the air, and solutions of ammonia and the fixed alkalis (Abstr., 1883, 282, 286), employing in recent experiments magnesium, aluminium, and tin. Magnesium exposed to the air in contact with aqueous potash, gave small quantities of nitrous acid, ozone, and hydrogen peroxide. With ammonia solution, strong indications of nitrous acid were obtained. Aluminium in potassium hydrate produced nitrous acid readily, even in the cold,

nitric acid and hydrogen peroxide were also easily detected. With ammonia the action was much slower. Tinfoil gave scarcely any reaction; nitrous acid was not produced, but hydrogen peroxide was perceptible. J. T.

Compounds of Arsenious Anhydride with Halogen Salts. By F. Rüdorff (*Ber.*, **19**, 2668—2679).—In this paper the preparation and properties of compounds of the halogen salts of the alkali metals with arsenious anhydride are described. These are best obtained by passing carbonic anhydride into a mixed solution of potassium arsenite and the halogen salt. These compounds separate either in the amorphous form or in indistinct crystals, of the general formula $MX,2As_2O_3$, sparingly soluble in water, insoluble in alkaline carbonates, but very soluble in the free alkalis; when heated, they decompose with elimination of arsenious anhydride, the compound $KI,2As_2O_3$ decomposing at 350°; $KBr,2As_2O_2$ at 300°; and KCl,As_2O_3 at 240°; a compound, $KCl,2As_2O_3$, is also described. The ammonium compounds NH_4I,As_2O_3, $NH_4Br,2As_2C_3$, and NH_4Cl,As_2O_3, are also described, those of sodium being reserved for a future communication.

V. H. V.

Some Probable New Elements. By A. Pringle (*Chem. News*, **54**, 167—168).—The author claims to have discovered some new substances, including five metals and a substance resembling selenium, called *hesperisium*, in some "Lower Silurian" rocks, situated in the county of Selkirk. One metal is said to be like iron, but gives neither the thiocyanate nor the tannic acid reaction; one is like lead in appearance, is easily fused and volatilised, and yields yellow and green salts; another which is charcoal-black, is called *erebodium;* its equivalent is 95·4, and it forms several oxides. A fourth, *gadenium*, with equivalent about 43·6, a light-grey powder, forms a red monoxide and a cream-coloured dioxide, yielding respectively white and yellow salts. Another, *polymnestum* (Pm), is a rather dark-coloured metal, with equivalent about 74. A preliminary description of four oxides, PmO, PmO_2, PmO_3, and (?) PmO_5, of two sulphides, PmS and PmS_2, and of other compounds is given. D. A. L.

Production of Alkali Metals. By H. Y. Castner (*Chem. News*, **54**, 218—219).—Iron reduced by hydrogen or carbonic oxide is mixed with tar in proper proportions, so that after the mixture is coked it has a composition about = FeC_2. The coke is finely ground, mixed with caustic soda (or potash) in proportions = $3NaHO + FeC_2$, or about 100 NaHO to 15 of coke. This mixture is introduced into a cast-iron crucible, and heated in a specially arranged furnace (described in the paper). The reduction and distillation commence at a temperature of 1000°. When the operation is finished the crucible is removed, and another immediately put in its place. The residue consists of some sodium carbonate, and finely divided iron; the sodium carbonate is recovered, the iron used to make fresh reducing coke, and the crucible is used over and over again. The advantages over the old method are manifest. D. A. L.

Crystalline Scale formed in the Manufacture of Sodium Hydrogen Carbonate. By G. W. Leighton (*Amer. J. Sci.*, **32**, 318—319).—This scale was formed in the manufacture of sodium hydrogen carbonate by the ammonia process, at Syracuse, New York. It was deposited on the inner surface of an iron tank, and had the appearance of boiler-scale, being 1 to 2 inches thick, with a vitreous lustre, and a greenish-grey colour. It is usually covered with crystal planes, proving to be the termination of prisms (probably monoclinic). Analysis gave the following results :—

NaCl.	Na_2CO_3.	$MgCO_3$.	$CaCO_3$.	$FeCO_3$.	H_2O.	CO_2.	Total.
22·23	40·62	31·57	3·56	0·08	0·63	0·64	99·33

The scale is evidently a triple salt, represented by the formula $MgCO_3,Na_2CO_3,NaCl$. It is, in fact, a definite crystalline product of an interesting constitution, not unlike that of several well-defined mineral species, in which an alkaline chloride appears to be in molecular combination with heterogeneous materials. B. H. B.

Strontia Dihydrate. By C. Heyer (*Ber.*, **19**, 2684—2690).—When strontium hydroxide is heated to bright redness, it is converted into strontium oxide. When the latter is exposed to air saturated with aqueous vapour, and then to dry air at the ordinary temperature, strontia dihydrate, $SrO,2H_2O$, is obtained as a white, crystalline powder.

Dry strontia dihydrate, when heated with dry carbonic anhydride, is completely converted into carbonate; the monohydrate, however, absorbs only traces of carbonic anhydride. The water in the dihydrate was determined by passing dry carbonic anhydride over the substance for five hours at 26·5°, and for 40 minutes at 121·5°, and absorbing the water in sulphuric acid bulbs. These results are not in accordance with those obtained by Scheibler (Abstr., 1886, 927).

N. H. M.

Calcium Borate. By B. Blount (*Chem. News*, **54**, 208—209).—The salt obtained by fusing freshly calcined lime with boric anhydride over a Bunsen burner is CaB_4O_7. It is possible that the salt obtained on a platinum wire loop before the blowpipe, with large excess of boric anhydride, contains a larger proportion of boric acid.

D. A. L.

Calcium Ammonium Arsenate and Calcium Arsenates. By C. L. Bloxam (*Chem. News*, **54**, 168—170; 193—194).—In a previous communication (Abstr., 1886, 920), mention is made of a calcium ammonium arsenate. Various observers differ as to the composition of this salt and as to the amount of water it contains. The amount of water appears to vary somewhat with the state of the atmosphere, and hence, probably, the cause of the difference of opinion on this point. It is now shown theoretically and experimentally that the precipitate produced by arsenic acid in a solution of calcium chloride containing free ammonia has the following composition :—

Air-dried..... $CaNH_4AsSO_4 + 7H_2O$.
Dried in a vacuum over sulphuric acid, $Ca_3NH_4H_2(AsO_4)_3 + 3H_2O$.
Dried at 100°..... $Ca_6NH_4H_5(AsO_4)_6 + 3H_2O$.
Ignited ..... $Ca_2As_2O_7$.

It is suggested to use the precipitation of calcium as calcium ammonium arsenate for quantitative purposes; it is convenient, the precipitate being crystalline and bulky, but is not susceptible of such great accuracy as the oxalate method. It is recommended for checking hardness determinations in water analysis. Its various advantages and disadvantages as a method are discussed. On evaporating down a hydrochloric acid solution of calcium ammonium arsenate with platinic chloride, the platinochloride after ignition was observed to be mixed with fine, white, opaque, prismatic crystals of the orthoarsenate $Ca_3(AsO_4)_2$, insoluble in acids. A repetition of the experiment resulted in the production of a substance somewhat similar in appearance, namely the meta-arsenate $Ca(AsO_4)_2$; the same substance is formed when mixtures of arsenious anhydride and calcium carbonate are ignited, and is left as an insoluble, crystalline powder when the ignited mass is treated with hydrochloric acid. D. A. L.

Artificial Lead Silicate from Bonne Terre, Missouri. By H. A. Wheeler (*Amer. J. Sci.*, **32**, 272—273).—E. S. Dana and S. L. Penfield have given (Abstr., 1886, 317) some crystallographic determinations and analyses of this artificial mineral from the Desloge Lead Co., of Bonne Terre. Since the publication of that paper, the author has examined some specimens in the metallurgical collection of Washington University. The results of his analysis are as follows:—

	SiO_2.	PbO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.
I	17·11	73·66	0·80	0·53	2·35	0·22
II	18·51	72·93	1·31	0·62	1·66	0·20

	Cl.	Na_2O.	NiO.	Total.
I	0·08	2·22	3·06	100·03
II	undet.	undet.	undet.	95·23

I, coarse crystals; II, fine crystals. The iron in these analyses was assumed to be in the form of ferric oxide. B. H. B.

Equivalent of Gadolinium Oxide. By A. E. Nordenskiöld (*Compt. rend.*, **103**, 795—798).—Gadolinium oxide is the mixture of yttrium, erbium, and ytterbium oxides, which was first obtained from the gadolinite found at Ytterby. It is precipitated by ammonia and ammonium oxalate as well as by potassium sulphate, and the three constituents cannot be separated quantitatively.

The gadolinium oxide obtained from kainosite, the silicocarbonate of yttrium, erbium, and ytterbium, recently discovered at Hitterö, in Norway, has the molecular weight 260·2 if O = 16 and the formula of the oxide is taken as M_2O_3. This number is practically identical with the molecular weight of the similar mixture of oxides obtained

by different observers (Nordenskiöld, Lindström, Engström, Clève) from gadolinite, kainosite, azzhenite, xenotime, fergusonite, clevite, fluocerite, and eudialite. These minerals are found in different localities, and contain the oxides in combination with different acids, such as silicic, phosphoric, niobic, or tantalic acid. Moreover, the oxides have been separated by somewhat different methods, and yet in all cases the greatest variation from the mean value for the molecular weight, 261·9, is one per cent., a variation which is within the error of experiment, and is not greater than the alterations which have been made in recent times in the atomic weights of some of the better known elements. It follows therefore that *gadolinium oxide, although not the oxide of a simple substance, but a mixture of three isomorphous oxides, has a constant molecular weight, even when obtained from totally different minerals found in widely separated localities.* This is the first instance of the coexistence of three isomorphous substances in constant proportions. The explanation of this fact seems to be a problem analogous to that of the origin of the minor planets.

C. H. B.

Formation of Ultramarine in the Wet Way. By F. Knapp (*J. pr. Chem.* [2], **34**, 328—340).—An account of some further experiments on the formation of ultramarine by the exposure of a heated mixture of kaolin, soda, and sulphur, to a damp atmosphere, or treatment of the same with liver of sulphur (Abstr., 1886, 306). The various conditions necessary for success are discussed in full, such as the degree of aggregation of the liver of sulphur and the form of silicate or silica used. Thus experiments with quartz were unsuccessful, and those with silicic acid jelly from soluble glass led to the production of a bluish-green material, which turned to a deep blue on warming. Pure alumina led to no result, but sodium aluminate gave a very satisfactory product. Salts of sodium, such as the thiosulphate, or even calcium phosphate, produced very fine specimens of ultramarine-blue.

V. H. V.

Sodium Dichromate. By A. Stanley (*Chem. News*, **54**, 194—196).—Sodium dichromate crystallises with 2 mols. H_2O, in prisms and plates belonging to the triclinic system; its sp. gr. is 2·5246 at 13°; it is deliquescent. It loses 1 mol. H_2O below 75°, and all below 100°, leaving a light brown, anhydrous salt, which fuses to a transparent dark red liquid at 320°, and on cooling crystallises in the same forms as the hydrated salt. When treated with water, the anhydrous salt causes a rise, and the hydrated salt a fall in temperature. 100 parts of the saturated aqueous solution contain—

Temperature..	0°	15°	30°	80°	100°	139°
Parts $Na_2Cr_2O_7$	107·2	109·2	116·6	142·8	162·8	209·7

The saturated solution boils at 139°. A table of the sp. gr. of solutions of various strengths is given. Sodium dichromate is insoluble in ether, slightly soluble in alcohol. It is very hygroscopic, in 48 hours an exposed sample absorbed one-third its weight of water; a sample of calcium chloride under similar circumstances absorbed

nearly its own weight of water. It decomposes slightly above its melting point, and at a dull red heat leaves sodium chromate and chromic oxide. In its reactions generally it resembles potassium dichromate.

By dissolving the dichromate in warm aqueous chromium trioxide, the trichromate separates on cooling in dark red crystals; these are very soluble in water, and are deliquescent.

By the action of sodium dichromate on freshly prepared cupric hydroxide, a brown powder is formed, consisting of microscopic crystals of the composition $Na_2CrO_4,CuCr_2O_7,2CuO + 4H_2O$. It is almost insoluble in water, and but slightly soluble in alcohol. It loses all its water below 100°, and partially decomposes at higher temperatures, cupric oxide separating.

Magnesium sodium chromate, prepared by neutralising sodium dichromate with magnesia, crystallises with 3 mols. H_2O, in yellow four-sided prisms and plates. It is soluble in water and alcohol, but insoluble in ether. The 3 mols. H_2O are driven off below 200°, leaving a dark reddish-brown powder, which fuses at a red heat with partial decomposition. D. A. L.

Reduction of Inorganic Thio-salts by Hydrogen. By G. Krüss and H. Solereder (*Ber.*, **19**, 2729—2739).—By the reduction of molybdothio-salts by hydrogen at a red heat, salts of a lower molybdosulphide could not be obtained; potassium thiomolybdate and ammonium dithiomolybdate are gradually reduced to a mixture of molybdenum and potassium sulphide and to molybdenum. In the case of ammonium dithiomolybdate, no oxysulphide could be obtained.

Potassium thallium sulphide, $K_2Tl_2S_4$, behaves in a similar manner, being reduced to potassium sulphide and thallium.

The salts of such thio-acids as remain unchanged in a current of hydrogen are not reduced; for example: $K_2S,3ZnS$; $K_2S,3CdS$, &c. If the thio-acid is merely reduced to a lower stable sulphide, the corresponding thio-salt yields also the lower sulphide or its thio-salt in the case of its having the properties of a thio-acid. Examples: $K_2S,3Cu_2S,Cu_2S_2$, K_2S,Fe_2S_3. N. H. M.

Atomic Weight of Tungsten. By J. Waddell (*Amer. Chem. J.*, **8**, 280—288).—Scheelite was decomposed by nitric acid, and the impure tungsten trioxide freed from silica as follows:—The mixture is fused with an equal weight of hydrogen potassium sulphate until in a state of limpid fusion; the cool mass is digested with water and filtered; water containing ammonium carbonate must be used for the further washing to keep the fluid from running through turbid, and to assist in the solution of the tungstate. If the silica is to be estimated it will probably require a second fusion, &c., with acid potassium sulphate. Another method of separating tungstic acid and silica is by means of ammonia, but here also the extraction is apt to be incomplete. Commercial metallic tungsten is but slowly attacked by acids, it cannot be fused with nitre without attacking the crucible, and is therefore best oxidised by a current of air at a red heat. The product is fused with sodium carbonate, and after dissolution

filtered from unoxidised material. The filtrate boiled with ammonium carbonate gave a small precipitate of alumina. To remove molybdenum, tartaric acid is added (half the weight), then hydrochloric acid (no tungstic acid is precipitated), and sulphuretted hydrogen passed. The blue filtrate is decolorised by a current of air, and the tungsten separated in 11 fractions by boiling with hydrochloric acid. Fractions 3, 7, and 10 were purified for determination of the atomic weight by solution in ammonia, reprecipitation by hydrochloric acid, and roasting of the precipitate in a current of air. The analysis was effected by heating gradually in a current of hydrogen, using a porcelain boat and tube, and a Fletcher's blast furnace. No. 3 gave W = 184·50, No. 7 184·00, and No. 10 183·67, when O = 16. The first number is to be considered most accurate, namely, W = 184·50, O = 16; or W = 184·64, O = 15·96. The specific gravity of this sample of metal is 18·77. H. B.

Compounds of Gold and Nitrogen. By F. Raschig (*Annalen*, **235**, 341—368).—*Aurous oxide*, Au_2O, is most conveniently prepared by boiling a solution of mercurous nitrate with an excess of auric chloride, as described by Figuier (*Ann. Chim. Phys.* [3], **11**, 336). The precipitate dried over phosphoric anhydride contains 2 mols. H_2O. When strong ammonia is added to water containing aurous oxide in suspension, a black explosive powder, NAu_3,NH_3, is obtained. Boiling with water, or with dilute acids, converts the *sesqui-auroamine* into *triauramine*, NAu_3. Methylamine also acts on aurous oxide, forming *diauromethylamine*, $NMeAu_2$. This compound also loses half its nitrogen when boiled in water for 15 minutes. Gold monoxide, AuO, was first obtained in a pure state by Schottländer (Abstr., 1883, 853). It is converted by strong ammonia into the very explosive compound *sesquihydraurylamine*, $NH_3,N(AuOH)_3$. Warm hydrochloric acid dissolves two-thirds of the gold, but one-third is left in the metallic state. On boiling with water, half the nitrogen is expelled, and *trihydraurylamine* remains. Methylamine unites with gold monoxide, forming the compound $MeN(AuOH)_2$; this loses half its nitrogen in the form of methylamine when boiled in water. The author confirms the accuracy of Dumas's formula, $(AuN+NH_3)_2+3H_2O$, for the fulminating gold prepared by the action of ammonia on auric oxide, Au_2O_3; but he proves that the substance which is precipitated by ammonia from a solution of auric chloride is a mixture of the preceding compound and *auric imidochloride*, NH:AuCl. The latter compound is obtained in an impure state when a few drops of ammonia are added to a large excess of auric chloride. Only a portion of the chlorine can be removed by digestion with ammonia.

Fulminating gold is slowly attacked by boiling water, losing ammonia. Boiling with nitric acid renders the compound more explosive. Dilute sulphuric acid does not liberate ammonia, but forms a very explosive substance of the composition $(AuN_2H_3)_4,H_2SO_4$.

The constitution of auric diamine is represented by the formula $NH_2{\cdot}Au:NH$. The decomposition it undergoes when boiled with water is probably $2NH_2AuNH = NH:AuN:AuNH_2 + NH_3$.

Methylamine yields a yellow precipitate with auric chloride, soluble

in an excess of the reagent. On warming the solution, a brown precipitate which contains a large quantity of chlorine is deposited. Auric oxide yields a red compound with methylamine.

W. C. W.

Complex Inorganic Acids. By W. Gibbs (*Amer. Chem. J.*, 8, 289—290).—Compounds have been obtained comparable with the chlorplatinophosphoric acids of Schutzenberger. These compounds are to be regarded as phosphoric acid in which one atom of oxygen is replaced by platinous chloride, bromide or oxide, or the corresponding compounds of palladium, iridium, ruthenium, and osmium. Moreover the phosphorus may be replaced by arsenic or antimony. The following formulæ are given to the compounds so far studied:—

$As_2O_3,3(As_2O_3,2PtO),5(NH_4)_2O + 7H_2O$;
$(As_2O_3,2PtCl_2)K_2O + 2H_2O$;
$24WO_3,As_2O_3,3(As_2O_3,2PtCl_2),12Pt(NH_3)_4O + 60H_2O$;
$22WO_3,3As_2O_3,3(As_2O_3,2PtO)6Pt(NH_3)_4O + 40H_2O$;
$12MoO_3,As_2O_3(As_2O_3,2PtO)2Pt(NH_3)_4O + 27H_2O$.

H. B.

Roseo-rhodium Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **34**, 394—406; compare Abstr., 1883, 1058).—*Roseo-rhodium nitrate*, $(Rh_2,10NH_3,2H_2O)(NO_3)_6$, is obtained by adding moderately dilute nitric acid to a concentrated solution of roseo-rhodium hydroxide, when it separates as a white precipitate consisting of microscopic, quadratic tables. It loses 2 mols. of water at 100°, and is converted into nitratopurpureo-rhodium nitrate. It is easily soluble in water.

Roseo-rhodium platinochloride nitrate, $(Rh_2,10NH_3,2H_2O)(NO_3)_2PtCl_6 + 2H_2O$, is obtained as a beautiful, orange-yellow, crystalline precipitate on adding hydrogen platinochloride to a solution of the nitrate. It easily loses 2 mols. of water at 100°, the other 2 mols. are given off more slowly, and nitratopurpureo-rhodium platinochloride is formed; on treating this with dilute hydrochloric acid all the platinum is dissolved, leaving white nitratopurpureo-rhodium chloride undissolved. A solution of the latter in water gives with sodium dithionate a precipitate of the characteristic nitratopurpureo-dithionate.

Roseo-rhodium bromide, $(Rh_2,10NH_3,2H_2O),Br_6$, is prepared by adding concentrated hydrogen bromide to a solution of roseo-rhodium hydroxide. It forms a crystalline powder consisting of small octohedrons or six-sided tables. At 100°, it loses 2 mols. H_2O and is converted into the bromopurpureo-bromide. It is easily soluble in cold water, and its aqueous solution gives the same reactions as the nitrate.

Roseo-rhodium sulphate, $(Rh_2,10NH_3,2H_2O)(SO_4)_3 + 2H_2O$, is prepared by saturating the hydroxide with dilute sulphuric acid, and precipitating with alcohol. It forms a white precipitate of very small octohedral crystals. In contrast to the other roseo-rhodium salts, it is not converted into the purpureo-salt by solution in boiling water; it crystallises in large, quadratic prisms, terminated by a quadratic pyramid, apparently isomorphous with roseocobalt sulphate. At 100°, it quickly loses 4 mols. H_2O, and then more slowly another $\frac{1}{2}$ mol., undergoing a similar change to the analogous roseocobalt salt, form-

ing luteo-salts. An aqueous solution gives all the reactions of the nitrate; with potassium iodide, it gives a white precipitate, consisting of microscopic octohedrons of the *roseoiodide sulphate*,

$$(Rh_2,10NH_3,2H_2O)I_2(SO_4)_2.$$

Roseo-rhodium platinochloride sulphate, $(Rh_2,10NH_3,2H_2O)PtCl_6(SO_4)_2$, is obtained as a beautiful, silky, buff precipitate of very thin six-sided tables, by adding a solution of hydrogen platinochloride to a cold solution of the roseo-sulphate. It seems to be isomorphous with the corresponding roseo- and luteo-salts of cobalt and chromium.

Roseo-rhodium orthophosphate, $(Rh_2,10NH_3,2H_2O)(PO_4H)_3 + 4H_2O$, is prepared by adding a 10 per cent. solution of phosphoric acid to a concentrated solution of the hydroxide. It forms a white, crystalline powder which behaves like the corresponding cobalt salt.

Sodium roseo-rhodium pyrophosphate, $(Rh_2,10NH_3,2H_2O),P_2O_7Na + 23H_2O$, is obtained by adding sodium pyrophosphate to a solution of the hydroxide in dilute hydrochloric acid until the amorphous precipitate at first formed is redissolved; on shaking, the salt then separates as a silky, white crystalline precipitate. It agrees in all respects with the cobalt salt.

Roseo-rhodium cobalticyanide, $(Rh_2,10NH_3,2H_2O),CO_2Cy_{12}$, is obtained as small pale-yellow crystals on adding a solution of potassium cobalticyanide to the hydroxide, neutralised with dilute sulphuric acid.

G. H. M.

Nitratopurpureo-rhodium Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **34**, 401—409).—*Nitratopurpureo-rhodium nitrate*,

$$(NO_3)_2(Rh_2,10NH_3)(NO_3)_4,$$

is easily obtained by heating the roseonitrate or by dissolving this salt in hot water, adding an equal volume of concentrated nitric acid, heating the mixture for some time on the water-bath and then allowing it to cool, when the salt separates in small, octohedral, white crystals with a greenish-yellow tinge. Heated over a flame, the salt explodes. It is only slightly soluble in water.

Nitratopurpureo-rhodium chloride, $(NO_3)_2(Rh_2,10NH_3)Cl_4$, is obtained as a pale greenish-yellow precipitate on filtering a cold solution of the nitrate into an ice-cold mixture of 3 vols. hydrochloric acid and 1 vol. water. An aqueous solution gives all the reactions of the nitrate.

Nitratopurpureo-rhodium dithionate, $(NO_3)_2(Rh_2,10NH_3)(S_2O_6)_2 + 2H_2O$, is prepared by precipitating a cold saturated solution of the nitrate or chloride with sodium dithionate. It forms white, silky X-shaped aggregations resembling the corresponding cobalt salt. The air-dried salt loses all its water at 100°. It is quite insoluble in water.

G. H. M.

Xantho-rhodium Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **34**, 410—423).—*Xantho-rhodium nitrate*, $(NO_2)_2(Rh_2,10NH)(_3NO_3)_4$, is prepared by dissolving the chloropurpureochloride in dilute sodium hydroxide on the water-bath, and then adding pure sodium nitrite and dilute nitric acid; the salt separates as a white, crystalline powder which can be recrystallised from hot water. Heated over a flame, the

salt explodes and leaves a voluminous residue of rhodium. The xanthonitrate is fairly soluble in cold, easily in hot water; insoluble in alcohol. Its aqueous solution, unlike that of the nitratonitrate, is not converted into the roseonitrate by boiling. It is also unacted on by sodium hydroxide, ammonium sulphide, &c.

Xantho-rhodium chloride, $(NO_2)_2(Rh_2,10NH_3)Cl_4$, is prepared in the same way as the nitrate, adding dilute hydrochloric acid, however, instead of nitric acid after the sodium nitrite, when the salt separates as a white powder; or from the nitrate, by filtering a concentrated solution of the latter into dilute hydrochloric acid, the addition of alcohol then throws down a yellowish-white precipitate of small octahedrons. When heated, the salt is decomposed, and leaves a residue of pure rhodium. Treated with silver oxide and water, the chloride yields a solution of *xantho-rhodium hydroxide*, which behaves as a strong alkali.

Xantho-rhodium platinochloride, $(NO_2)_2(Rh_2,10NH_3)(PtCl_6)_2$, is obtained as a buff-coloured precipitate consisting of microscopic needles by adding hydrogen platinochloride to a solution of the nitrate. This salt is analogous to the corresponding cobalt and chromium salts.

Xantho-rhodium bromide, $(NO_2)_2(Rh_2,10NH_3)Br_4$, is obtained as a white, crystalline precipitate on adding concentrated hydrobromic acid to a cold solution of the nitrate. It is easily soluble in water, and the solution gives all the reactions of the nitrate.

Xantho-rhodium dithionate, $(NO_2)_2(Rh_2,10NH_3)(S_2O_6)_2 + 2H_2O$, is prepared by filtering a cold solution of the nitrate into an excess of sodium dithionate. It forms a white, crystalline precipitate consisting of microscopic prisms. It loses all its water at 100°.

Xantho-rhodium sulphates are prepared by treating the chloride with strong sulphuric acid, &c. (*a*) The *normal* salt,

$$(NO_2)_2(Rh_2,10NH_3)(SO_4)_2,$$

crystallises in flat, brilliant, needles many centimetres long. It may also be obtained by precipitating a solution of the acid salt with alcohol. The salt explodes on heating. With a solution of iodine in potassium iodide, it yields a periodide.

(*b*) The *acid* salt, $2[(NO_2)_2(Rh_2,10NH_3)(SO_4)_2],(H_2SO_4)_3$, crystallises in long, white needles. The salt decomposes quietly on heating, leaving the rhodium in pseudomorphs of the crystals.

Xantho-rhodium silicofluoride, $(NO_2)_2(Rh_2,10NH_3)(SiF_6)_2$, is obtained as a snow-white, silky precipitate on adding a cold solution of the nitrate to an excess of hydrofluosilicic acid. Under the microscope, it consists of small rhombic tables resembling the chloropurpureo-rhodium silicofluoride. Dilute nitric acid decomposes it, forming the nitrate and free acid.

Xantho-rhodium oxalate, $(NO_2)_2(Rh_2,10NH_3)(C_2O_4)_2$, is obtained as a white precipitate consisting of microscopic prisms, by adding a solution of the nitrate to excess of ammonium oxalate. Nitric acid decomposes it in the same way as the silicofluoride.

The roseo- and purpureo- as well as the xantho-salts of rhodium show a most unmistakable resemblance to those of cobalt and chromium. The xantho-rhodium salts are, however, much more stable

than those of cobalt and chromium. The nitrate is especially so, showing that the xantho-salts are really nitritopurpureo-salts. The great stability of the nitrate is partly accounted for by the nature of the metal, and also probably partly by the fact that pentad nitrogen is combined with pentad nitrogen, thus:—

$$\begin{matrix} O:N\cdot O \\ \quad\| \\ O:N\cdot O \end{matrix}\!\!>(Co_2,10NH_3)(NO_3)_4.$$

G. H. M.

Mineralogical Chemistry.

Twin Crystal of Molybdenite. By W. E. Hidden (*Amer. J. Sci.*, **32**, 210).—This crystal was found near Renfrew, Canada, with other remarkable crystals, some of which weighed nearly a pound. The method of twinning seems to prove that molybdenite should be referred to the hexagonal system. B. H. B.

Limonite-pseudomorphs after Iron Pyrites. By J. G. Meem (*Amer. J. Sci.*, **32**, 274—276).—These limonite pseudomorphs are found near Lexington, Rockbridge Co., Virginia, occurring in the soil. In colour they vary from light-brown to almost black. Most of the crystals have undergone a complete alteration, there being no iron pyrites visible to the naked eye. In some, the unaltered iron pyrites is found forming a nucleus at the centre, in others it forms the bulk of the crystal. The most common form of these pseudomorphs is the octahedron; this generally occurs combined with the cube. On nearly all the octahedral faces, striations running at right angles to the edges of these faces are observed. (Compare Abstr., 1886, 992.) B. H. B.

Brookite from Magnet Cove, Arkansas. By E. S. Dana (*Amer. J. Sci.*, **32**, 314—317).—S. L. Penfield (Abstr., 1886, 989) described a crystal of brookite of unusual form, from Magnet Cove. The author has studied the large series of brookite crystals from this locality in the collection of C. S. Bement. The planes he has determined on these crystals are as follows:—Pinacoids, $\infty\breve{P}\infty$, 0P; prisms, $\infty\breve{P}2$, ∞P, $\infty\breve{P}2$, new; brachydome, $2\breve{P}\infty$; pyramids, $\frac{1}{2}P$, $\frac{1}{2}\breve{P}2$, $\frac{3}{4}P\frac{3}{2}$, 1P2. B. H. B.

Turquois from New Mexico. By F. W. Clarke and J. S. Diller (*Amer. J. Sci.*, **32**, 211—217).—At Los Cerillos, New Mexico, about 22 miles south-west of Santa Fé, are mines of turquois which have been worked for centuries. The turquois has never been fully analysed. It occurs buried in its matrix, sometimes in nodules, often in veins. It varies in colour from pure sky-blue to dark-green. For analyses, three typical samples were selected—1, bright blue, faintly translucent; 2, pale-blue, opaque, earthy, sp. gr. 2·805; 3, dark-green, opaque. The results were as follows:—

H_2O.	Al_2O_3.	Fe_2O_3.	P_2O_5.	CuO.	SiO_2.	CaO.	Total.
19·80	39·53		31·96	6·30	1·15	0·13	98·87
19·60	36·88	2·40	32·86	7·51	0·16	0·38	99·79
18·49	37·88	4·07	28·63	6·56	4·20	—	99·83

In discussing these results, it is advisable to compare them with the figures given by Church for the Persian variety (*Chem. News*, **10**, 290), and with those given by Moore (Abstr., 1885, 958) for Californian turquois, pseudomorphous after apatite. These analyses, ignoring the dark-green variety (3), agree well with each other in their atomic ratios. The turquois is shown by these analyses to be a variable mixture of the salts, $2Al_2O_3,P_2O_5,5H_2O$, and $2CuO,P_2O_5,4H_2O$. The former formula may be regarded as that of normal turquois, and may be within $Al_2HPO_4(OH)_4$. The copper salt to which the mineral owes its colour is to be considered as an impurity, a view confirmed by the analysis of the dark-green variety (3).

A microscopic study of the turquois indicates that the mineral may have been derived from the alteration of another substance (apatite) with which the vein was formerly filled. The turquois-bearing rock appears to be eruptive, and probably of tertiary age. Under the microscope, it is seen to be composed of felspar, with a considerable amount of biotite, epidote, iron pyrites, limonite, and some amorphous substance. B. H. B.

A Remarkable Crystal of Herderite. By W. E. Hidden (*Amer. J. Sci.*, **32**, 209).—This crystal was found at the locality near Stoneham, Maine (Abstr., 1884, 827, 1102). Excepting 3P2, ∞P$\breve{2}$, and ∞P$\breve{3}$, all the planes observed in the American crystals occur on this crystal, and one new plane, P$\bar{\infty}$, is seen to be present. The crystal has a diameter of 25 mm., and in point of size and perfection is unequalled. The planes occurring are 13 in number, with several others slightly indicated. The mean index of refraction for this species for yellow rays is found by Des Cloizeaux to be 1·609. B. H. B.

Pseudomorphs of Garnet. By S. L. Penfield and F. L. Sperry (*Amer. J. Sci.*, **32**, 307—311).—Pseudomorphs of garnet occur in abundance in a bed of chloritic schist overlying the great magnetite bed of the Spurr-Michigamme iron range. The crystals are invariably dodecahedral, varying in sp. gr. from 4·11 to 3·22; the heaviest crystals being nearly pure garnet, and the lightest ones almost wholly the decomposition product. Analysis of the garnet and of the decomposition products gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.
I.	38·03	20·83	—	36·15	2·14	0·97	2·73
II.	27·45	19·53	6·26	29·42	—	6·04	—
III.	29·08	19·94	3·91	30·48	0·20	5·56	0·25

	Na_2O.	K_2O.	H_2O.	Total.
I.	—	—	—	100·85
II.	0·42	2·64	7·50	99·26
III.	0·29	3·66	6·53	99·90

I, pure garnet; II, decomposition product from a crystal having a sp. gr. of 3·281; III, the same from a crystal having a sp. gr. of 3·22. The decomposition product appears to be closely related to Sandberger's aphrosiderite. The material in which the garnets are embedded is a ferriferous chlorite, differing from the alteration product of the garnet, and agreeing closely with thuringite.

The pseudomorph garnets from Salida, Chaffee Co., Colorado, differ from the Lake Superior garnets in that the decomposition product forms only a coating, whilst the interior of the crystal is quite homogeneous. The following are analyses (I) of the pure garnet, sp. gr. 4·163, and (II) of the decomposition product, after deducting 1·04 per cent. of garnet:—

	SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.
I.	37·61	22·70	33·83	1·12	3·61	1·44
II.	28·20	22·31	19·11	—	17·68	0·48

	Na_2O.	K_2O.	H_2O.	Total.
I.	—	—	—	100·31
II.	0·72	1·03	10·90	100·43

The changes which have been previously noted in garnet, differ from those described by the authors, in that they have been the alteration of pyrope into ripidolite or serpentine-like magnesium silicates.

B. H. B.

Phenacite from Colorado. By W. E. Hidden (*Amer. J. Sci.*, **32**, 210—211).—Since the original announcement of the discovery by the author, of phenacite at Florissant (Abstr., 1885, 878), many additional crystals have been found; the best of them being sent to Professor Des Cloizeaux for examination. He observed 12 planes, amongst which $\frac{1}{2}P2$ is new for this species. B. H. B.

North Carolina Mineral Localities. By W. E. Hidden and A. Des Cloizeaux (*Amer. J. Sci.*, **32**, 204—208).—*Spodumene* has been discovered in Sharpe's Township, Alexander Co. Physically the emerald-green spodumene (hiddenite) found, is identical with the yellow spodumene (triphane) of Brazil. The three indices of refraction were found to be: $\alpha = 1{\cdot}677$; $\beta = 1{\cdot}669$; $\gamma = 1{\cdot}651$ for yellow rays.

Black tourmaline, noteworthy from the brilliancy and number of the planes presented, occurs at the same locality. Twelve planes have been identified.

Xenotime was discovered about 3 miles east of the Emerald and Hiddenite Mine, in Alexander Co. The colour of the crystals is hair-brown, and some of them are perfectly transparent. Sp. gr. 4·45 to 4·52. The cleavage is prismatic, and the habit long prismatic.

Twin crystals of monazite occur with the xenotime. Few finer examples of this rare mineral have ever been found. The crystals are transparent, red, and highly polished. They vary in size from 4 to 20 mm. in length and thickness. They are prismatic from an unusual extension of $+P$ and $+\bar{P}\infty$. A distinct but imperfect cleavage parallel to the clinopinacoid was observed on several crystals, whilst

the common basal cleavage was absent. The fact that common monazite is described as having perfect basal cleavage suggests that the difference may be due to the thorium silicate often present as an impurity.

Quartz crystals with basal plane.—Genuine basal planes are of very rare occurrence in the so-called basal-plane quartz crystals from North Carolina. In most cases, the planes observed have been produced by compression or juxtaposition, and when carefully measured do not meet the requirements. B. H. B.

Mica from Leon Co., Texas. By G. W. Leighton (*Amer. J. Sci.*, **32**, 317—318).—This mica attracted notice, as it presents characters intermediate between those of the vermiculites and the muscovites. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CuO.	Na_2O.	K_2O.	H_2O.	Total.
48·95	25·17	9·40	1·69	trace	trace	11·08	4·31	100·60

This composition agrees very closely with that of the mica from Hirschburg. It appears to be an early stage in the alteration of muscovite to vermiculite. B. H. B.

Ceriferous Hainstadt Clays. By J. R. Strohecker (*Chem. News*, **54**, 207—208).—The author replies to the criticisms of Blomstrand and of Schertel (Abstr., 1886, 678) and re-affirms the correctness of his statements (Abstr., 1886, 314, 424) as to the presence of the cerium metals in these clays.

Crystalline Structure of Iron Meteorites. By O. W. Huntington (*Amer. J. Sci.*, **32**, 284—303).—From an exhaustive study of the very large collection of meteorites at Harvard College, the author concludes that many of the masses of meteoric iron now known are cleavage crystals, broken off probably by the impact of the mass against the atmosphere. These masses show cleavages parallel to the planes of all the three fundamental forms of the isometric or regular system. The Widmanstätten figures and Neumann lines are sections of planes of crystalline growth parallel to the same three fundamental forms of the isometric system. On different sections of meteorites, Widmanstätten figures and Neumann lines can be exhibited in every degree with no break where a natural line of division can be drawn. The features of the Widmanstätten figures are due to the elimination of incompatible material during the process of crystallisation.

The results of this investigation confirm the theory that the process of crystallisation must have been very slow; the most probable theory of the origin of meteorites seems to be that these masses were thrown off from a sun among the fixed stars, and that they were slowly cooled, while revolving in a zone of intense heat. B. H. B.

New Meteoric Iron from Texas. By W. E. Hidden (*Amer. J. Sci.*, **32**, 304—306).—This meteorite was found in 1882, in Maverick Co., Texas. It weighs 97¼ lbs., and measures 12 by 10 by 6 inches

in its three diameters; its shape being a nearly symmetrical ovoid, somewhat flattened. The surface is quite smooth, and coated with the usual thin black crust. When a small surface is etched a peculiar appearance was presented. There are no Widmanstätten figures, except in traces. There are, however, two series of fine lines, crossing each other at angles of 70° and 110°, which the author concludes to be due to twinning lamellæ. The metal is of unusual whiteness, and is very soft. Analysis gave the following results :—

Fe.	P.	Ni + Co.	Total.	Sp. gr.
94·90	0·23	(4·87)	100·00	7·522

B. H. B

Meteoric Iron from Glorieta Mt., New Mexico. By G. F. Kunz (*Amer. J. Sci.*, **32**, 311—313).—Since the publication of the account of the three masses of meteoric iron from Glorieta Mt. (Abstr., 1886, 321), three more masses of the meteorite have been found by J. H. Bullock, and a small piece was found by a Mexican, but it disappeared before it could be secured. Seven fragments have thus far been obtained. No. 4 weighs 2·65 lbs.; No. 5, 2·48 lbs.; and No. 6, 2·31 lbs. All these fragments are figured and described by the author.

A meteorite was recently presented to the Colorado Scientific Society by the Boston and Colorado Silver Mining Company, who received it from Albuquerque, Mew Mexico, as silver bullion. Its weight before cutting was about 5 lbs. An analysis of the iron gave the following results :—

Fe.	Ni.	Co.	Cu.	Zn.	C.	P.	S.	Si.	Total.
88·76	9·86	0·51	0·03	0·03	0·41	0·18	0·01	0·04	99·83

The striking similarity between this analysis and that of the Glorieta meteorite, leads the author to believe that this iron is the seventh fragment of the meteorite found by the Mexican, and mistaken by him for silver bullion. B. H. B.

Two hitherto undescribed Meteoric Stones. By E. S. Dana and S. L. Penfield (*Amer. J. Sci.*, **32**, 226—231).—1. *Meteorite from Utah.*—This was found in 1869, in the prairie between Salt Lake City and Echo, and is now in the Yale collection. Its weight is 875 grams. It is oblong in shape, about 12 cm. long, and 9 cm. in its greatest width. The surface is comparatively smooth; the colour of the crust being reddish-black. The interior of the stone is of a dark bluish-grey colour, distinctly mottled by its chrondritic character, and showing a rather large proportion of iron irregularly distributed through it, with minute patches of troilite. Olivine is the most prominent constituent. Bronzite appears in irregular crystal fragments scattered through the mass, and plagioclase felspar is sparingly present in crystalline fragments. The sp. gr. of the meteorite was found to be 3·66. Analysis gave 17·16 per cent. of nickeliferous iron, and 82·84 per cent. of the mineral part, including the troilite and silicates. The iron gave on analysis—

Fe.	Ni.	Co.	Cu.	Total.
91·32	8·04	0·60	0·04	100·00

The mineral portion was divided into:—Soluble in hydrochloric acid; troilite, 6·70 per cent. with 0·62 of NiS; silicates, 48·85 per cent. Insoluble in hydrochloric acid, including chromite, 43·97. Water, 1·14. Total, 100·66.

Analyses of the soluble (I) and insoluble (II) portions gave:—

	SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.
I.	40·33	0·51	21·33	35·15	1·66	0·33
II.	54·83	4·82	8·64	24·56	3·34	1·98

	K_2O.	P_2O_5.	Chromite.	Total.
I.	0·04	0·65	—	100·00
II.	0·12	—	1·71	100·00

The composition of the insoluble part implies that it is made up of bronzite with a little plagioclase. The Chantonnay meteorite seems to bear the closest resemblance to the new stone.

2. *Meteorite from Cape Girardeau, Missouri.*—This stone fell at 3 P.M., on August 14, 1846, accompanied by a loud report. It became the property of the Yale Museum several years ago. The stone in the museum consists of two parts fitted together, and weighing together 2058 grams. The general shape of the stone is roughly rectangular, with dimensions of 12 by 10 by 10 cm. The surface is smooth, and, where fresh, is of a light grey colour. The metallic particles are scattered uniformly through the mass. The chondritic character is distinct. The sp. gr. of the stone was found to be 3·67. The analysis showed a relation of native iron to troilite and silicates very near that of the Utah meteorite, namely, 17·90 to 82·10 per cent. The iron gave on analysis—

Fe.	Ni.	Co.	Cu.	Total.
91·93	7·39	0·63	0·05	100·00

The analysis of the mineral portion gave:—Soluble in hydrochloric acid: troilite, 6·95; silicates, 42·68. Insoluble in hydrochloric acid, including chromite, 50·19. Water, 0·58. Total 100·40. The soluble (I) and insoluble (II) parts gave—

	SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.
I.	36·32	—	22·31	40 23	—	0·28
II.	55·79	5·54	7·91	23·65	3·35	1·85

	K_2O.	P_2O_5.	Chromite.	Total.
I.	0·04	0·82	—	100·00
II.	0·24	—	1·67	100·00

The insoluble part is evidently bronzite, with some felspar. The stone belongs to the light grey chondrite type of meteorites.

B. H. B.

Organic Chemistry.

Methods for Determining the Relative Stability of the Alkyl Bromides. By I. Remsen and H. W. Hillyer (*Amer. Chem. J.*, **8**, 251—262).—The bromides in molecular proportion were treated in alcoholic solution with the several reagents, and the hydrobromic acid formed estimated by silver nitrate solution with ferric thiocyanate as indicator. The relative results are embodied in the following table, Column I showing the action of zinc and dilute sulphuric acid; II, the action of cobalt-zinc couples and acetic acid; III and IV, the action of alcoholic soda under certain conditions; V, the action of cobalt-zinc couples in presence of soda, but after deducting the action of the soda itself; VI, that of ammonia; and VII, that of silver nitrate or acetate. The action of sodium amalgam is unsatisfactory, owing to the constant variation of the alkalinity of the solution, and the authors believe that the best results are to be obtained by the action of caustic soda or ammonia, or of silver salts.

	I.	II.	III.	IV.	V.	VI.	VII.
Ethyl bromide	0·8	1·3	28·4	81·2	1·0	—	—
Propyl „	1·0	3·3	9·7	65·2	1·11	27·3	2·6
Butyl „	3·6	6·0	4·3	25·2	0·58	—	—
Iso-propyl bromide	8·8	11·1	3·4	15·7	0·53	4·3	21·7
Amyl bromide	4·5	9·5	4·5	33·4	0·83	—	—

H. B.

Derivatives of Diethylene Bisulphide. By W. Mansfield (*Ber.*, **19**, 2658—2668).—In continuation of former work (Abstr., 1886, 525), other derivatives of diethylene bisulphide, $C_4H_8S_2$ (compare Masson, Trans., 1886, 234), are described.

The methiodide, $C_4H_8S_2,MeI$, is converted by silver chloride into the corresponding chlorine compound, a crystalline substance melting at 225°; it yields crystalline precipitates with platinic, mercuric, and auric chlorides. With moist silver oxide, the methiodide yields the corresponding hydroxide, $C_4H_8S_2Me{\cdot}OH$, the solution of which possesses well-marked basic properties, absorbs carbonic anhydride, and precipitates solutions of the heavy metals. The salts obtained by its neutralisation with acids are exceedingly deliquescent; the most stable is the picrate, which crystallises in golden needles melting at 192—193°. The dimethiodide, $C_4H_8S_2,2MeI$, melts at 207—208°, and yields a corresponding chloro-derivative, which gives precipitates with the chlorides of the platinum-group of metals. In the course of the preparation of the dimethiodide, a periodide of the composition $C_4H_8S_2MeI,I_2$ is obtained, which melts at 92—93°, and crystallises in the monoclinic system ($a : b : c = 0{\cdot}89 : 1 : 0{\cdot}67$).

Experiments made with a view of obtaining the hydroxides by

evaporation of their aqueous solutions were unsuccessful; an oil of composition $C_5H_{10}S_2$ was formed (to this substance Masson ascribes the formula $C_{12}H_{24}S_5$, *ibid.*, 247). The author considers that this compound is derived from dithioglycocine by the displacement of both sulphydryl hydrogen-atoms by the methyl and vinyl groupings respectively, thus, $SMe{\cdot}C_2H_4{\cdot}S{\cdot}CH:CH_2$; and in accordance with this view it is shown that the compound takes up four atoms of bromine. Diethylene bisulphide combines readily with benzyl halogen compounds; thus with the bromide it forms a substance, $C_4H_8S_2,C_7H_7Br$, which melts at 146°, and crystallises in the rhombic system. The corresponding iodine compound crystallises in pale yellow needles, decomposing when heated at 145°, and the chlorine compound in colourless needles melting at 143°. On heating the above bromine compound with alkalis, an oil of the composition $C_{11}H_{24}S_2$ is produced.

V. H. V.

Disulphones. By R. Escales and E. Baumann (*Ber.*, **19**, 2814—2817).—*Ethylidenediethylsulphone*, $CHMe(SO_2Et)_2$, is prepared by the action of potassium permanganate on α-dithioethylpropionic acid (from pyruvic acid and mercaptan). It forms plates rather soluble in water, more soluble in alcohol and ether. It melts at 60°, and distils without decomposition. The *bromo-derivative*, $CBrMe(SO_2Et)_2$, crystallises in small prisms melting at 115°; it is sparingly soluble.

Ethylidenediphenylsulphone, $CHMe(SO_2Et)_2$, is prepared by gradually treating a very dilute solution of potassium dithiophenylpropionate (Abstr., 1886, 878) with 1 per cent. permanganate solution. It is insoluble in water, alkalis, and acids, sparingly soluble in alcohol and ether, more readily in benzene. It melts at 101—102°. It is isomeric with Blomstrand and Ewerloeff's ethylenediphenylsulphone (*Ber.*, **4**, 716; compare also Otto and Damköhler, *J. Pharm. Chem.*, **30**, 171 and 321).

N. H. M.

Disulphones. By E. Baumann (*Ber.*, **19**, 2806—2814).—*Diethylsulphonedimethylmethane*, $CMe_2(SO_2Et)_2$, is prepared by shaking dithioethyldimethylmethane with 5 per cent. permanganate solution, and occasionally adding a few drops of acetic or sulphuric acid. When no more permanganate is decolorised, the liquid is heated and filtered, and the filtrate evaporated to half its bulk. The greater part of the disulphone separates on cooling. It crystallises in thick prisms, melts at 130—131°, and boils with slight decomposition at about 300°. It is readily soluble in warm alcohol and water, rather soluble in ether, benzene and chloroform. Sulphuric acid dissolves it very readily, and decomposes it when warmed; nitric acid and bromine both dissolve it, but are without further action.

Diethylsulphonepropylmethylmethane, $CMePr(SO_2Et)_2$, crystallises from water in long needles melting at 86°; it dissolves sparingly in water, readily in alcohol, ether, and chloroform.

Ethylic β-diethylsulphonebutyrate, $CMe(SO_2Et)_2{\cdot}COOEt$, is prepared by oxidising ethylic β-dithioethylbutyrate. It crystallises from water in slender needles more than an inch long, melts at 63°, and dissolves very sparingly in cold water, more readily in alcohol and ether.

Diethylsulphonemethane, $CH_2(SO_2Et)_2$, is obtained by oxidising ethyl orthothioformate (Gabriel, this Journal, 1877, ii, 311) with potassium permanganate in presence of sulphuric acid. It crystallises in lustrous plates melting at 104°; and dissolves sparingly in ether, readily in benzene and alcohol. When the aqueous solution is treated with bromine-water, the *dibromo-derivative*, $CBr_2(SO_2Et)_2$, is formed. This crystallises from boiling water in lustrous needles melting at 131°.

The disulphone is probably formed by the oxidation of the sulphide $CH_2(SEt)_2$ present in the thio-ether. N. H. M.

Reagent for the Hydroxyl-group. By H. A. Landwehr (*Ber.*, **19**, 2726).—The substance to be tested is added in excess to 10 to 20 c.c. of a solution of ferric chloride (prepared by adding two drops of a 10 per cent. solution of ferric chloride to 60 c.c. of water) contained in a white dish. The production of a sulphur colour denotes the presence of hydroxyl. All hydroxy-acids and all alcohols and carbohydrates which dissolve in water give the reaction. Ether, alkyl salts, formic, propionic, butyric, oxalic, fumaric, and malonic acids give negative results. N. H. M.

Non-acid Constituents of Beeswax. By F. Schwalb (*Annalen*, **235**, 106—149).—Repeated boiling with alcohol extracts about 5 per cent. of cerotic acid from beeswax. The residue is saponified with alcoholic soda, and after the alcohol has been removed by distillation and by boiling with water, the soap is separated by the addition of common salt. To remove any free alkali, the soap is pressed in a cloth, redissolved in hot water, and again salted out. This operation is repeated several times. The soap is thoroughly dried at 110—120°, and the non-acid constituents are separated by fractional solution in, and recrystallisation from, light petroleum. The most soluble portion of the extract, melting between 55° and 65°, contains two hydrocarbons; one melting at 60·5° appears to be identical with Krafft's normal heptacosane, $C_{27}H_{56}$ (Abstr., 1882, 1273), and the other which melts at 67°, is probably identical with normal hentriacontane, $C_{31}H_{64}$. It is probable that other hydrocarbons are also contained in the wax.

The myricyl alcohol is less soluble in light petroleum than the hydrocarbons. It appears to have the formula $C_{31}H_{64}O$, and is not identical with the alcohol $C_{30}H_{62}O$, contained in carnauba wax (Abstr., 1884, 1281). It melts at 85—85·5°, and resolidifies at 84°. When heated with soda lime, it is converted into the salt of an acid, $C_{31}H_{62}O_2$. This acid is sparingly soluble in the usual solvents at the ordinary temperature, but it dissolves in hot light petroleum, and is deposited from the solution in white needle-shaped crystals, which melt at 88·5—89°. The lead salt melts at 115—116°, and dissolves freely in acetic acid and in boiling toluene. The silver salt is amorphous. It melts at 180°, with decomposition. The copper and magnesium salts are also amorphous. They dissolve in boiling benzene. The methyl and ethyl salts crystallise in needles. They dissolve freely in warm

ether and warm alcohol. The methyl salt melts at 71—71·5°, and the ethyl salt at 69·5—70°. Heated under the ordinary atmospheric pressure, the ethyl salt decomposes before boiling into ethylene and the free acid.

Beeswax also contains two lower alcohols, namely, ceryl alcohol, $C_{26}H_{54}O$ or $C_{27}H_{56}O$, and an alcohol of the formula, $C_{24}H_{50}O$ or $C_{25}H_{52}O$. W. C. W.

Conversion of Starch into Glucose by means of Hydrochloric Acid. By S. Harvey (*Analyst*, **11**, 221—223).—In reference to the process used by Heisch, heating in a boiling water-bath is as good as heating over a naked flame. In the author's experiments, whenever the conversion of starch was complete, the results obtained were too low, owing to destruction of the glucose; in fact, it appears impossible to limit the time of heating, so as to prevent the glucose being attacked. D. A. L.

Carbohydrates. By M. Hönig and S. Schubert (*Monatsh. Chem.*, **7**, 455—484).—In a former paper (Abstr., 1886, 44), the authors have shown that by the action of sulphuric acid on cellulose and starch, a series of sulphuric acid-derivatives are formed of the general composition $C_{6n}H_{10n}O_{5n-x}(SO_4)_x$. These are decomposed in alcoholic solution with production of sparingly soluble compounds, containing a smaller proportion of sulphuric acid, which in their turn are decomposed at a higher temperature with formation of various dextrins. The different phases of these changes in the case of cellulose, starch, and grape-sugar are worked out more fully in this paper. From cellulose, a series of derivatives is obtained from a form of soluble cellulose to dextrose, according to the temperature (5—33°) at which the change is effected; these increase in specific rotatory power and solubility, the lower members of the series giving a blue coloration with iodine, the intermediate a red, and the end products no coloration, corresponding with the formation of an achroodextrin. These substances also differ from one another as regards their conversion by diastase; the end members are unaltered, whilst the others are converted into dextrins.

From starch, a similar series of compounds was obtained; although in this case the specific rotatory power diminishes from that of starch to that of a dextrin similar to the final product from cellulose, but differing from it in possessing a slight cupric oxide reducing power.

With grape-sugar also, similar results were obtained.

In conclusion, the question is discussed whether the starch molecule is compounded of other less complex units, differing among themselves, a view represented by the formula $15(C_{12}H_{20}O_{10})$, assigned by Brown and Heron, or whether it is decomposed into these less complex molecules by a chemical change rather than by a process of disintegration. V. H. V.

Identity of Cadaverine with Pentamethylenediamine. By A. Ladenburg (*Ber.*, **19**, 2585—2586).—Cadaverine and pentamethylenediamine show the same boiling point, solubility and odour,

and agree in their general reactions. The mercuriochloride of pentamethylenediamine has the formula $C_5H_{14}N_2,2HCl,3HgCl_2$, whilst, according to Brieger, that of cadaverine mercuriochloride is

$$C_5H_{14}N_2,2HCl,4HgCl_2.$$

The imine obtained from cadaverine is identical in its properties with piperidine, which the author has previously shown to be the imine of pentamethylenediamine (Abstr., 1886, 139, 269).

W. P. W.

Compounds of Aldehydes and Ketones with Mercaptan. By E. Baumann (*Ber.*, **19**, 2803—2806).—When furfuraldehyde and mercaptan are treated with dry hydrogen chloride, the reaction is accompanied by considerable development of heat, which causes a further decomposition. Fatty aldehydes and ketones and aromatic aldehydes also react with mercaptan with development of heat; with fatty aromatic ketones, the mixture must be warmed, whilst in the case of benzophenone the reaction only takes place in presence of zinc chloride.

When dithiophenyldimethylmethane, $CMe_2(SPh)_2$ (Abstr., 1885, 749), is prepared, avoiding development of heat, a solid product is obtained instead of an oil. It forms large, clear crystals, which melt at 56°, and dissolve readily in alcohol, ether, benzene, &c., and are insoluble in water. When heated at 100°, it decomposes into a mixture of several substances, which no longer solidifies. Dithioethyldimethylmethane, $CMe_2(SEt)_2$ (*loc. cit.*), was also prepared at a lower temperature, and was obtained as a mobile, strongly refractive liquid, boiling at 190—191°; it combines directly with methyl iodide, yielding a crystalline substance.

N. H. M.

Linoleic Acid. By K. Peters (*Monatsh. Chem.*, **7**, 552—555).—The formula generally ascribed to linoleic acid is $C_{16}H_{28}O_2$; it would thus be the isologue of palmitic acid, and convertible into it by hydrogenising agents. It is here shown that the analytical results of a sample of an acid, purified by means of its barium salt, are more in accordance with the formula $C_{18}H_{32}O_2$, and when heated with phosphorus and hydriodic acid, it yields not palmitic, but stearic acid.

V. H. V.

Acetyllævulinic Acid. Constitution of γ-Ketonic Acids. By J. Bredt (*Annalen*, **236**, 225—232).—Acetyllævulinic acid is formed by the action of acetic anhydride on lævulinic acid at 100°. It is deposited from an alcoholic solution in crystals, resembling those of potassium nitrate. It melts at 78—79°, and boils about 140°, under 15 mm. pressure; under the ordinary atmospheric pressure, it splits up on boiling into acetic acid and α- and β-angelica lactones.

As the compound is neither decomposed by water nor by a cold solution of sodium carbonate, the author regards it as a hydroxylactone-derivative, not as an anhydride. This is evidence in favour of the formula $CH_2<\begin{matrix}CH_2\text{–}\\CO\cdot O\end{matrix}>CMe\cdot OH$ for lævulinic acid.

W. C. W.

New Reaction of Aluminium Chloride; Syntheses in the Acetic Series. By A. COMBES (*Compt. rend.*, **103**, 814—817).—When aluminium chloride is added to a solution of acetic chloride in carbon bisulphide or chloroform, there is abundant evolution of hydrogen chloride, and a white, crystalline solid of the composition $C_{12}H_{14}O_6Al_2Cl_8$ is obtained. It remains unaltered in dry air, but is immediately decomposed by water with evolution of carbonic anhydride. If the water is added carefully to the solid, or if the latter is thrown into water in small quantities at a time, a clear liquid is obtained, which, when extracted with ether, or better, chloroform, yields a colourless liquid boiling at 136—137° under a pressure of 750 mm. It has the composition $C_5H_8O_2$, and is lighter than water, in which it is readily soluble without undergoing any decomposition. The action of aluminium chloride on acetic chloride is represented by the equation—

$$6C_2H_3OCl + Al_2Cl_6 = 4HCl + (COMe{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CCl_2O{\cdot})_2Al_2Cl_4,$$

and the solid compound is decomposed by water with formation of aluminium hydroxide and the acid $COMe{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$, which immediately loses carbonic anhydride and yields acetylacetone, $C_5H_8O_2$.

Acetylacetone has the properties of a diketone, and combines, with development of heat, with a concentrated solution of sodium hydrogen sulphite. It is not affected by phosphorous chloride or acetic chloride, but is decomposed by potash or soda, with formation of acetone and an acetate. When treated with sodium amalgam, it yields isopropyl alcohol, pinacone, and sodium acetate. If slowly hydrogenised in an acid solution, it should yield symmetrical amylic isoglycol, $CH_2(CHMe{\cdot}OH)_2$. Bromine acts energetically on acetylacetone, with formation of acetic bromide and penta- and tetra-bromacetone. Phosphoric chloride removes the oxygen, and yields a tetrachloride which immediately loses 2 mols. HCl, and yields chlorides of the composition $C_5H_6Cl_2$, derived from an unknown valerylene.

When the solid product of the action of aluminium chloride on acetic chloride is treated with absolute alcohol instead of water, no gas is evolved. The products will be described in a subsequent paper.

This reaction is general, and takes place with propionic and butyric chlorides, and with chloral. C. H. B.

Gluconic Acids. By F. VOLPERT (*Ber.*, **19**, 2621—2623).—*Ethylic pentacetylgluconate* is a white, crystalline substance, readily soluble in alcohol and water; it melts at 103·5°. Ammonium and potassium gluconate crystallise well in plates and needles. Comparative experiments made with Hoenig's paragluconic acid (Abstr., 1881, 893) show that it is identical with gluconic acid.

N. H. M.

Action of Thiocarbamide on Ethyl Acetoacetate. By R. LIST (*Annalen*, **236**, 1—32).—In the preparation of thiomethyluracil from thiocarbamide and ethyl acetoacetate, by the process previously described by the author (Abstr., 1886, 443), it is found that the pre-

sence of ammonium thiocyanate increases the yield of the product. *Thiomethyluracil*, $CS<^{NH\cdot CMe}_{NH\cdot CO-}>CH$, is very sparingly soluble in alcohol, ether, and cold water. It crystallises in plates, and begins to decompose at 280°. The silver and copper salts are amorphous. The mercuric salt forms anhydrous, microscopic needles. The potassium salt, $C_5H_5N_2OSK + \frac{1}{2}H_2O$, is insoluble in alcohol, but freely soluble in water. The sodium salt, $C_5H_5N_2OSNa + 2H_2O$, crystallises in prisms, which effloresce on exposure to the atmosphere. The methyl salt melts at 219—220°, but begins to sublime at 120°, forming plates or needle-shaped crystals. The addition of silver nitrate to the ammoniacal solution of this substance precipitates the compound $C_6H_7N_2SOAg$. The ethyl compound melts at 144—145°.

Ethyl thiomethyluracilacetate is obtained in needle-shaped crystals by the action of ethyl monochloracetate on thiomethyluracil. *Thiomethyluracilacetic acid* crystallises in needles or plates, and melts at 203—204°. It is very sparingly soluble in cold water, alcohol, and ether.

Thiomethyluracil unites with hydrogen bromide to form an unstable crystalline additive product. Bromine acts on thiomethyluracil suspended in water, eliminating the sulphur and forming dibromoxymethyluracil. By a similar reaction, dichloroxymethyluracil is obtained in transparent plates, soluble in hot water and in warm alcohol. Thiomethyluracil is converted into methyluracil by boiling with freshly precipitated silver or mercuric oxide, and also by the action of ammonia or strong hydrochloric acid at 150°, and of acetic acid at 180°. W. C. W.

Nitro-derivatives of Methyluracil. By A. Köhler (*Annalen*, **236**, 32—57).—Behrend (*Annalen*, **229**, 32) obtained nitrouracilcarboxylic acid and a compound, $C_5H_2N_4O_5$, by the action of strong nitric acid on methyluracil. Nitrouracilcarboxylic acid, $C_5H_3N_3O_6 + 2H_2O$, crystallises in rhombic prisms; $a : b : c = 0{\cdot}323 : 1 : 1{\cdot}081$. On boiling the aqueous solution, carbonic anhydride is evolved and nitrouracil, $C_4H_3N_3O_4$, is formed. *Ethyl nitrouracilcarboxylate*, prepared by saturating the alcoholic solution of the acid with hydrogen chloride, crystallises in monoclinic prisms. It is less soluble in alcohol and water than the free acid, and it does not split up on boiling with water. The salt melts at about 250° with partial decomposition. The constitution of this substance may be represented by the formula $NH<^{CO\text{——}NH}_{CO\cdot C(NO_2)}>C\cdot COOEt$.

Amidouracilcarboxylic acid, $C_5H_5N_3O_4$, is formed by the action of tin and hydrochloric acid on the nitro-acid, but a better yield is obtained by the reduction of the ethyl salt. The product, consisting of a mixture of the ethyl salts of amidouracilcarboxylic and hydroxyuracilcarboxylic acids, is saponified by boiling with an aqueous solution of potassium hydroxide. Amidouracilcarboxylic acid is deposited from its aqueous solution in needles. Between 150° and 160°, it splits up into carbonic anhydride and amidouracil. The potassium salt, $C_5H_6N_3O_5K + H_2O$, crystallises in prisms; the barium,

copper, and mercury salts are amorphous. The sparingly soluble lead and silver salts are crystalline. The ethyl salt is insoluble in alcohol and sparingly soluble in water. It melts at 260° with partial decomposition.

A good yield of nitrouracil is obtained by adding 5 c.c. of strong sulphuric acid to 4 grams of methyluracil suspended in 10 c.c. of fuming nitric acid. The yield of the sparingly soluble compound, $C_5H_2N_4O_5$, which is obtained as a bye-product by the action of nitric acid on methyluracil, is increased by warming the mixture as soon as the reaction ceases.

This compound unites with bases to form salts. $C_5HN_4O_5{\cdot}NH_4 + \frac{1}{2}H_2O$ crystallises in yellow glistening needles; $C_5HN_4O_5K + 1\frac{1}{2}H_2O$, red needles, sparingly soluble in water; the solution decomposes on boiling. The barium salt, $(C_5HN_4O_5)_2Ba + 4H_2O$, forms prismatic needles, freely soluble in water. On reduction with tin and hydrochloric acid, the amido-compound, $C_5H_4N_4O_3 + H_2O$, is obtained in slender needles, sparingly soluble in water. After evaporation with hydrochloric acid, the residue yields the murexide reaction.

W. C. W.

New Mode of Formation of Dibromo- and Dichloro-barbituric Acids. By R. Behrend (*Annalen*, **236**, 57—68).—The most convenient method of preparing bromomethyluracil (Abstr., 1886, 338) is to convert methyluracil into dibromoxymethyluracil by the action of bromine-water (*Annalen*, **229**, 18), and to decompose the product by boiling in alcohol. *Dichloroxymethyluracil* resembles the corresponding bromo-derivative in its properties and in its mode of preparation. It crystallises in triclinic plates, and is not decomposed by boiling with alcohol. It is decomposed by alcohol or water at 150°, forming a sparingly soluble compound, and is converted into monochloromethyluracil by the action of stannous chloride and hydrochloric acid. Chloromethyluracil is insoluble in ether, sparingly soluble in water and alcohol. It crystallises in needles.

Dibromoxymethyluracil is oxidised to *dibromobarbituric* acid by fuming nitric acid. This is identical with the dibromobarbituric acid described by Baeyer (*Annalen*, **130**, 130). Hot fuming nitric acid converts dichloroxymethyluracil into *dichlorobarbituric acid*, $C_4H_2Cl_2N_2O_3$. This substance crystallises in rhombic prisms or plates, $a : b : c = 0{\cdot}7766 : 1 : 0{\cdot}8929$. The crystals are isomorphous with those of dibromobarbituric acid, and are much more soluble in alcohol, ether, and water. A small quantity of barbituric acid is formed in the preparation of dichlorobarbituric acid by this process.

W. C. W.

Relation of the so-called α-Thiophenic Acid to the Normal Thiophencarboxylic Acids. By V. Meyer (*Annalen*, **236**, 200—224).—In former communications (Abstr., 1885, 1207; 1886, 227, 534), the author has pointed out that the derivatives of α- and β-thiophenic acids (melting at 118° and at 126·5° respectively), are identical in crystalline form, solubility, and melting point, but that on decomposition the α-derivatives yield the α-acid, and the β-derivatives the β-acid. The so-called α-acid is really a mixture of the β- and γ-acids, which cannot be separated by recrystallisation. It is formed on

oxidising a mixture of β- and γ-thiotolens, but is not obtained by mixing together the ready-formed β- and γ-acids. In the thiophen-group the tendency for the isomeric compounds to crystallise together is much stronger than in any other series. W. C. W.

Halogen Carriers. By C. Willgerodt (*J. pr. Chem.* [2], **34**, 264—292).—An account of experiments on the effective value of various elements and their compounds in the chlorination of benzene (compare Abstr., 1885, 1034). Two cases occur on the passage of chlorine into benzene in presence of these foreign substances, namely, either the formation of benzene hexachloride attended by a considerable gain in weight of the benzene and practically no evolution of hydrogen chloride, or the displacement of hydrogen by chlorine with corresponding evolution of hydrogen chloride. The details of the various experiments are given in full. To the substances inducing the first reaction belong aluminium hydroxide and sulphate; those inducing the latter reaction are again separable into those elements the presence of which induces the production of mono- or di-substitution-derivatives, and those forming a chloride of the formula XCl_3 or $(XCl_2)_n$, which lead to the production of tetra- or penta-substitution-derivatives. The function of these is conditioned by the atomic mobility of the chlorine-atoms in its compound, and in fact to the affinity of some kind or another of the inorganic chloride for the carbon compound. Adopting the periodic system of classification, the members of the first two groups are inactive, those of the second, fifth, seventh, and eighth groups are eminently active, and those of the fourth are, with the exception of tin, inactive.

The experiments of Lothar Meyer, Friedel and Crafts, and others on the chlorination of carbon compounds by means of such substances as aluminium or ferric chloride, seem to indicate that at first a hydrogen-atom of the hydrocarbon is displaced by the grouping M_2Cl_5 with separation of hydrogen chloride, and to this compound a molecule of chlorine adds itself on and finally takes the place of the hydrogen. The compounds $Al_2Cl_6,6C_6H_6$ (or $6C_7H_8$) obtained by Gustavson, the author regards as combinations of a molecule of metallic chloride with one of the hydrocarbon, the remaining five molecules functioning in like manner to water of crystallisation. V. H. V.

Preparation of Organic Fluorides. By O. Wallach (*Annalen*, **235**, 255—271).—*Fluorobenzene*, C_6H_5Fl, can easily be prepared by pouring 20—30 c.c. of strong hydrofluoric acid into a flask containing 10 grams of benzene diazopiperidide. The flask is connected with a receiver by means of a spiral condenser surrounded by a freezing mixture. A tube passes through the doubly perforated cork which closes the receiver, and dips into mercury. On gently warming the flask, the reaction commences and the fluorobenzene collects in the receiver. *Fluorotoluene* is prepared from toluene paradiazopiperidide. As it is much easier to condense than fluorobenzene, the apparatus may be simplified by omitting the tube dipping under mercury. Fluorotoluene resembles benzonitrile in odour. It is oxidised by chromic acid, yielding fluorobenzoic acid.

Nitrobenzeneparadiazopiperidide forms golden, needle-shaped crystals. It melts at 96—97°, and dissolves freely in ether and warm alcohol. It is decomposed by hydrofluoric acid, yielding *parafluoronitrobenzene.* This compound is also formed by nitrating fluorobenzene. It melts at 21—22° and boils at 204—206°.

Acetamidobenzene metadiazopiperidide, $C_6H_4(NHAc)N : N_2C_5H_{10}$, is deposited from weak alcohol in thick prisms which melt at 100—101°. It is decomposed by hydrofluoric acid, yielding *metafluoraniline;* an oily liquid resembling aniline. *Parafluoraniline* is formed by reducing an alcoholic solution of parafluoronitrobenzene with stannous chloride and hydrochloric acid. The nitrate, hydrochloride, and sulphate crystallise well. Acetic anhydride converts parafluoraniline into *acetofluoranilide.* This compound is sparingly soluble in water, but dissolves readily in alcohol.

The replacement of hydrogen by fluorine increases the sp. gr., but has very slight effect on the boiling points of the compounds.

	Sp. gr.	B. p.
Benzene	0·899	80·5°
Toluene	0·882	111
Nitrobenzene	1·2	205
Aniline	1·036	184
Fluorobenzene	1·024	84—85
Parafluorotoluene	0·992	116°
Parafluoronitrobenzene	1·326	205—206
Parafluoraniline	1·153	185—189

Fluorobenzenesulphonic acid and fluorodiphenyl, when added to an alkaline solution of piperidine, form the compounds

$$NaSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_5NH_{10}$$

and $C_5NH_{10}{\cdot}N_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}C_5NH_{10}$ respectively. W. C. W.

Reaction of Potassium Cyanide with Orthonitrobenzylic Chloride. By E. Bamberger (*Ber.*, **19**, 2635—2642).—In the reaction between potassium cyanide and orthonitrobenzylic chloride there are formed, besides orthonitrobenzyl cyanide, an orthodinitrocyanodibenzyl and substances of the composition $C_{22}H_{14}N_4O_5$ and $C_{15}H_9N_3O_3$, the constitution of which is uncertain.

Orthonitrobenzyl cyanide, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, previously described by Salkowski, crystallises in pale-yellow prisms which melt at 82·5° ; its solutions give a blue-violet coloration on addition of a trace of alkali ; the dye formed is, however, unstable.

Orthodinitrocyanodibenzyl, $NO_2{\cdot}C_6H_4{\cdot}CH(CN){\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, crystallises in snow-white prisms, melts at 110·5° and is soluble in benzene, alcohol, and acetic acid. This substance is also obtained directly from orthonitrobenzyl chloride and the corresponding cyanide. It is very stable towards acids ; when heated with alkalis and the product heated with mineral acids, a compound, $C_{15}H_9N_3O_3$, separates out in voluminous, yellow flocculæ, which can be crystallised from alcohol in silky leaflets melting at 235—238°. The same substance is also a subsidiary product in the above reaction.

The compound $C_{22}H_{11}N_4O_5$, mentioned above, crystallises in thick glistening prisms which melt at 190·5°; it is sparingly soluble in alcohol, readily in acetic acid; it behaves towards acids and alkalis as a perfectly indifferent substance. V. H. V.

Oxidation of Nitromesitylene. By W. H. Emerson (*Amer. Chem. J.*, **8**, 268—271).—Schmitz has pointed out that as paranitromesitylenic acid is produced during the preparation of mononitromesitylene, it is probable that the first-named substance is produced by the oxidation of the last-named, and therefore here as in other cases, except with mesitylene sulphonamide, the presence of the nitro-group protects those hydrocarbon side-chains that occupy the ortho-position relatively to the negative nitro-group. This oxidation has before been attempted but without success; by dissolving both the substance and the chromic acid in glacial acetic acid, however, the paranitromesitylenic acid was actually obtained and recognised by its properties and by those of the corresponding amido-acid. H. B.

Intramolecular Changes in the Propyl-group of the Cumene Series. By O. Widman (*Ber.*, **19**, 2769—2780).—*Propylhydrocarbostyril*, $C_{12}H_{15}NO$, is obtained by treating a solution of orthamidocumenylacrylic acid (Abstr., 1886, 465) in soda with an excess of sodium amalgam. Acetic acid is then added, which precipitates a yellow substance melting at 80°; this changes in a short time to propylhydrocarbostyril melting at 134°. The latter crystallises in well-formed rhombic prisms, $a : b : c : = 0{\cdot}87978 : 1 : 1{\cdot}64451$; $\beta = 1{\cdot}620435$, and is very readily soluble in alcohol and benzene. The compound is also obtained by reducing orthamidoparapropylcinnamic acid (Abstr., 1886, 464). In the latter reaction, the isopropyl-group must have undergone an intermolecular change; propylhydrocarbostyril is therefore a normal compound of the formula

$$CH_2Me{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}CH_2{\cdot}CH_2\\ -NH{\cdot}CO-\end{matrix}{>}.$$

Cumenylpropionic acid (Perkin, this Journal, 1877, i, 400) is best prepared by boiling pure cumenylacrylic acid for 45 minutes with 20 times its weight of hydriodic acid (sp. gr. 1·7) and an equal weight of red phosphorus. The product is filtered, washed with water, and dissolved in ammonia; it is precipitated with acid, pressed, and dried. It melts sharply at 75·5° (not 70°). When gradually treated with fuming nitric acid (10 parts) at −5° to 0°, and the product poured into water, a white crystalline *nitro-acid* is precipitated; it crystallises from 50 per cent. acetic acid in well-formed plates melting at 99°. When reduced, it yields propylhydrocarbostyril. When cumenylpropionic acid is oxidised by potassium permanganate, it is converted into orthonitrohydroxyisopropylbenzoic acid (Abstr., 1886, 466).

The above experiments show that a conversion of isopropyl into normal propyl occurs in the successive conversion of cumenylacrylic acid into cumenylpropionic acid, orthonitrocumenylpropionic acid, and propylhydrocarbostyril. The same molecular change also takes place when cumenylacrylic acid is converted successively into

orthonitrocumenylacrylic acid, orthamidocumenylacrylic acid, and propylhydrocarbostyril. The author considers that the so-called "cumenylpropionic acid" contains normal propyl, and that it is *parapropylhydrocinnamic acid*. The propionic radicle, therefore, as well as the methyl and acrylic acid radicles, influences a propyl-group in the para-position, causing the formation of normal propyl.

N. H. M.

Reciprocal Transformations of Cymene- and Cumene-derivatives. By O. Widman (*Ber.*, **19**, 2781—2785).—With regard to the change of cumene- into cymene-derivatives, the author objects to Fileti's suggested law (this vol., p. 36) on the ground that the nature of the group has not been determined in any of the compounds containing these elements or groups (Cl, Br, Cy, COOH, &c.), and mentions experiments previously described by him (Abstr., 1886, 464) which show Fileti's view to be quite incorrect. N. H. M.

Octylbenzene. By F. Ahrens (*Ber.*, **19**, 2717—2725).—Octylbenzene (v. Schweinitz, Abstr., 1886, 540) boils at 262—264° (uncorr.), sp. gr. 0·852 at 14°. It solidifies at −7° to a crystalline mass, is insoluble in water, miscible with alcohol, ether, and benzene. *Chloroctylbenzene*, $C_6H_4Cl\cdot C_8H_{17}$, is prepared by the action of chlorine in presence of iodine on the hydrocarbon. It is a yellowish oil, almost without odour, readily soluble in alcohol and ether; it boils at 270—275°. *Bromoctylbenzene*, $C_6H_4Br\cdot C_8H_{17}$, boils at 285—287°. The *moniodo-derivative* is prepared by the action of iodine and mercury oxide on octylbenzene diluted with light petroleum. It is a yellow oil, insoluble in water, soluble in alcohol and ether. It solidifies at −4°, and does not distil without decomposition. It is very susceptible towards light and heat. *Metanitro-octylbenzene*, $NO_2\cdot C_6H_4\cdot C_8H_{17}$, is formed by the action of fuming nitric acid on octylbenzene in the cold. It crystallises in long needles insoluble in water and ether; sparingly soluble in alcohol and chloroform; it melts at 123—124°, and sublimes unchanged at a high temperature. When oxidised with potassium permanganate, it yields metanitrobenzoic acid. *Orthonitro-octylbenzene* is obtained, together with the para-derivative, by heating the mother-liquor from the preparation of the meta-compound. The heavy oil so formed is washed with hot water. It is a thick, yellow oil with a peculiar aromatic odour. It begins to decompose at 100°, and cannot be distilled; at 130° it suddenly carbonises. *Paranitro-octylbenzene* is obtained by first nitrating octylbenzene in the cold, separating the liquid from the crystals of metanitro-octylbenzene, and heating for 12 hours. It is then filtered and again heated, and this is repeated until all the hydrocarbon has dissolved. The crystalline substance is gently heated to sublime any metanitro-derivative present, and then strongly heated, when the para-compound sublimes. It forms small, yellowish, lustrous needles, having a slight odour of benzaldehyde; it melts at 204°, is insoluble in water, soluble in alcohol and ether. *Dinitro-octylbenzene*,

$$C_6H_3(NO_2)_2\cdot C_8H_{17},$$

was formed when crystals of metranitro-octylbenzene containing

fuming nitric acid were washed with ether. Water was poured on to stop the violent reaction which at once took place. It melts at 226°, and sublimes below this temperature in transparent crystals with a vitreous lustre, soluble in ether and alcohol, insoluble in water; its constitution was not determined. *Orthamido-octylbenzene hydrochloride*, $NH_2 \cdot C_6H_4 \cdot C_8H_{17}$,HCl, is prepared by reducing the nitro-compound with tin and hydrochloric acid; it forms small, lustrous, white plates; when heated, it becomes red. N. H. M.

A Fourth Monobromophenol, and a Second Monobromobenzene. By F. Fittica (*Ber.*, **19**, 2632—2634).—In this communication, the author still maintains the existence of the fourth monobromophenol described by him in a former work, the conclusions from which were subsequently shown by Hand to be erroneous (Abstr., 1886, 1017). The preparation of a second monobromobenzene is also described, but it was not obtained of constant boiling point (60—66°), and the analytical results are far from satisfactory. V. H. V.

Constitution of Nitranilic Acid. By R. Nietzki (*Ber.*, **19**, 2727).—When diamidotetrahydroxybenzene (obtained by reducing nitranilic acid) is distilled with zinc-dust, paraphenylenediamine is formed. This is fresh evidence that nitranilic acid is paradinitrodihydroxyquinone (compare Hantzch, Abstr., 1886, 1021). N. H. M.

Aniline and its Homologues. By L. Lewy (*Ber.*, **19**, 2728—2729; compare Abstr., 1886, 872).—When paratoluidine is boiled with water, splendid crystals of the *hydrate* separate on cooling; when exposed to air they effloresce.

The xylidines and cumidines behave towards phosphoric acid as orthotoluidine does, and yield only primary phosphates.

As paratoluidine forms a secondary phosphate, and orthotoluidine a primary phosphate, the para-compound behaves like an element having the atomic weight 214, whilst the ortho-compound behaves like an element having the atomic weight 107. In estimating the phosphoric acid in a mixture of the two phosphates, the relative amounts of paratoluidine and orthotoluidine can therefore be determined. N. H. M.

Alkyl-derivatives of Aniline. By A. Claus and H. Hirzel (*Ber.*, **19**, 2785—2791).—*Methylpropylaniline*, NPhMePr, is prepared by heating methylaniline and propyl iodide for eight hours in a water-bath. The product is dissolved in water, extracted with ether, and treated with alkali. It is a yellowish oil, boiling at 212° (uncorr.). The *hydrochloride* melts at 106° (uncorr.); it is very hygroscopic. The *ethiodide*, NPhMePr,EtI, is a viscous substance readily soluble in water. When boiled with concentrated aqueous potash, methylethylaniline is formed.

Ethylpropylaniline, NPhEtPr, is obtained by the action of propylaniline (Claus and Roques, *Ber.*, **16**, 909) on ethyl bromide, or from ethylaniline and propyl bromide. It is a bright yellow oil boiling at

216° (uncorr.). The *hydrochloride* is a crystalline substance, and melts at 131° (uncorr.). The *methiodide* is a syrup having all the properties of methylpropylaniline ethiodide.

Methylethylaniline was prepared by the method of Claus and Howitz (Abstr., 1884, 1005); it was obtained in the crystalline state. The *hydrochloride* melts at 114°. The propiodide is identical with the iodide mentioned above. When the aqueous solution of the iodide is heated, or kept in contact with ether, decomposition takes place, with formation of propyl alcohol and methylethylaniline hydriodide.

N. H. M.

Action of Ethyl Imidocarbonate on Aromatic Ortho-compounds. By T. Sandmeyer (*Ber.*, **19**, 2650—2657).—In continuation of former experiments on the reactions between ethyl imidocarbonate and the amines of the aromatic series (Abstr., 1886, 611), the preparation and properties of various derivatives of phenylene and toluylene diamines are described.

Ethoxymethenyltoluylenediamine, $C_7H_6<^{NH}_{N}>C\cdot OEt$, prepared from toluylenediamine hydrochloride and ethyl imidocarbonate, crystallises in golden needles which melt at 163°, insoluble in cold, sparingly soluble in hot water, moderately soluble in alcohol. Its aqueous solution gives a voluminous, white precipitate with mercuric chloride. With acids, it forms very soluble salts.

When heated with hydrochloric acid, it yields *hydroxymethenyltoluylenediamine*, $C_7H_6<^{NH}_{N}>C\cdot OH$. This substance crystallises in small needles, melts at 290°, and is sparingly soluble in boiling alcohol, readily in water. From its formation, it would seem to contain the hydroxyl-group, but it is also identical with a compound obtained directly from carbamide and toluylenediamine, which would contain the carbonyl-group; the atomic transformation of the —N—COH-group into —NH—C : O is however of frequent occurrence.

Ethoxymethenylphenylenediamine, $C_6H_4<^{NH}_{N}>C\cdot OEt$, prepared in like manner from phenylenediamine, crystallises in reddish glistening leaflets which melt at 160°. In its solubility and physical properties, it resembles its homologue. With hydrochloric acid, it yields hydroxymethenylphenylenediamine, $C_6H_4<^{NH}_{N}>C\cdot OH$, which crystallises in leaflets, and is identical with phenylenecarbamide obtained directly from orthonitrophenylurethane.

Ethoxymethenylamidophenol, $C_6H_4<^{O}_{N}>C\cdot OEt$, prepared from amidophenol and ethyl imidocarbonate, is a colourless oil, boiling at 225—230°, of peculiar odour. It is converted by hydrochloric acid into *hydroxymethenylamidophenol*, $C_6H_4<^{O}_{N}>C\cdot OH$, crystallising in red prisms, which lose their colour on exposure or when separating slowly from solution.

The reaction of the amido-acids on ethyl imidocarbonate differs

from those of the amines and the amidophenols; thus with anthranilic acid an amidine of the composition

$$COOH\cdot C_6H_4\cdot NH\cdot C(OEt):N\cdot C_6H_4\cdot COOH$$

is formed. This crystallises in white needles, melts at 223°, and is sparingly soluble in boiling water, soluble in hot alcohol. It would appear from its formation that this substance should be a bibasic acid, yet its silver salt contains only one atom of the metal in the molecule. V. H. V.

Decomposition of Diazo-compounds by Alcohol: Paradiazotolueneorthosulphonic Acid. By I. Remsen and A. G. Palmer (*Amer. Chem. J.*, 8, 243—251).—The authors expected to be able to prepare benzoic sulphinide by the oxidation of orthotoluenesulphonamide, itself prepared from the orthotoluenesulphonic acid obtained by boiling the diazo-compound of paramidotolueneorthosulphonic acid with alcohol. This method seemed all the more promising, as Jensen and Ascher have described the actual elimination of the diazo-group in the above compound.

The authors find no difficulty in the conversion of paranitrotoluene into paradiazotolueneorthosulphonic acid; but this, when boiled with alcohol under pressure, yields, contrary to the statements of Jensen and Ascher, not tolueneorthosulphonic acid as the principal product, but ethoxytolueneorthosulphonic acid. The reaction will not proceed without the application of pressure; it commences at 90 mm., and the two compounds are then formed in equal quantities, but the yield is very bad, the reaction slow, and the product is black with tarry matters. At 150 mm. thrice as much of the ethoxy-compound as of the toluenesulphonic acid is formed, and at 500 mm. the ethoxy-compound is formed almost alone; the reaction takes only a few minutes, and the product is far purer. The acid product of the reaction cannot be purified by means of the barium salts, but has to be converted into the acid amide, and it is to be noted that ethoxytoluenesulphamide, $OEt\cdot C_6H_3Me\cdot SO_2NH_2$ [4 : 1 : 2], melts at 143—144°, and not at 136°, as described by Heffter.

This action has not been satisfactorily explained. It is at present assumed by all writers that the normal reaction of the diazo-compounds when boiled with alcohol is that which results in the displacement of the diazo-group by hydrogen; it is, however, certain that the reaction frequently takes place in such a way as to form phenetoïls: thus the sulphate or nitrate of diazobenzene yields benzene in extremely small quantity, but phenetoïl in very considerable quantity, and it appears probable that the normal reaction is the one that gives the phenetoïl. A list of 15 similar cases is cited in illustration.

The action in the above case is therefore represented not by the equation generally given, but by

$$C_6H_3Me<^{SO_3}_{N_2}> + EtOH = OEt\cdot C_6H_3Me\cdot SO_3H + N_2.$$

H. B.

Diazo- and Diazoamido-compounds. By O. Wallach (*Annalen*, **235**, 233—255).—Some of the diazo-compounds of the monacetic derivatives of the diamines (Abstr., 1883, 584) are quite stable in the dry state, and their hydrobromides can be obtained in a pure state owing to their relatively slight solubility in water and alcohol. Acetic anhydride decomposes the dry diazo-compounds, yielding the acetic derivative of a phenol, thus acetoparatoluidine orthodiazobromide yields diacetamidocresol, $OAc{\cdot}C_6H_3Me{\cdot}NHAc$. The diazo-compounds unite with nitro-ethane to form the mixed azo-compounds discovered by V. Meyer (this Journal, 1875, 1202, and 1876, ii, 93), and they also combine with secondary amines, forming diazoamido-compounds. The latter substances are decomposed by boiling with strong hydrochloric, hydrobromic, and hydriodic acids according to the equation $RN:N{\cdot}NR'' + 2HCl = RCl + N_2 + NHR'',HCl$. Phenols are the chief products of the action of dilute sulphuric acid on the mixed diazoamido-compounds.

Benzene diazopiperidide, $C_5NH_{10}{\cdot}N_2{\cdot}Ph$, first described by Baeyer and Jaeger (this Journal, 1876, i, 273), can be readily prepared by pouring a dilute ice-cold solution of diazobenzene chloride (from 100 parts of aniline) into a dilute cold aqueous solution of piperidine, 100 parts by weight mixed with 60 of potassium hydroxide. Every precaution must be taken to prevent the temperature of the mixture rising above 0°. The piperidide melts at 43°. It is decomposed by warm hydrochloric, hydrobromic, and hydriodic acids, yielding chloro-, bromo-, or iodo-benzene respectively, and piperidine.

Toluene paradiazopiperidide, $C_6H_4Me{\cdot}N_2{\cdot}C_5NH_{10}$, crystallises in colourless prisms. It is soluble in alcohol, light petroleum, and ether, and melts at 41°. It unites with 2 mols. HCl to form an unstable compound. *Toluene orthodiazopiperidide* and *orthonitrotoluene paradiazopiperidide* are oily liquids. *Paranitrotoluene orthodiazopiperidide* melts at 50—51°, and is decomposed by hydrobromic acid, yielding bromonitrotoluene, $C_6H_3MeBr{\cdot}NO_2$ [1 : 2 : 4]. *Nitrobenzene metadiazopiperidide* and *benzene diazoconine* and *toluene paradiazoconine* are oily liquids.

By the action of sodium nitrite on a solution of acetotoluylenediamine in hydrobromic acid, the diazobromide,

$$NHAc{\cdot}C_6H_3Me{\cdot}N_2Br\ [Me : N_2Br : NHAc = 1 : 2 : 4]$$

is obtained as a yellow precipitate. In the dry state, this diazobromide is remarkably stable. It acts on an alcoholic solution of nitroethane and sodium ethoxide, yielding a red precipitate of *acetoparatoluidine orthodiazonitroethane*,

$$NHAc{\cdot}C_6H_3Me{\cdot}N_2{\cdot}CHMe{\cdot}NO_2\ [Me : N_2C_2H_4NO_2 : NHAc = 1 : 2 : 4].$$

The precipitate dissolves in alkalis, and is reprecipitated by acids. It is deposited from an ethereal alcoholic solution in red needles melting at 143°.

Acetoparatoluidine orthodiazodiethylamide, $NHAc{\cdot}C_6H_3Me{\cdot}N_2{\cdot}NEt_2$, is deposited in colourless prisms when acetoparatoluidine orthodiazobromide is added to a cold solution of diethylamine. It melts at 108°.

Acetoparatoluidine orthodiazopiperidide melts at 154°, and dissolves in alcohol and in ether. When hydrogen chloride is passed into the alcoholic solution, the diazochloride, $NHAc{\cdot}C_6H_3Me{\cdot}N_2Cl$, is precipitated in a state of purity. In a dry state, the diazochloride is stable. It explodes when heated, and is decomposed by boiling with water or weak alcohol, yielding acetamidocresol. The diazopiperidide is decomposed by warm hydrochloric or hydrobromic acid, yielding orthochloro- or orthobromo-acetoparatoluidine and monochloro- or monobromotoluidine. W. C. W.

Hydrazines. By E. Fischer (*Annalen*, **236**, 198—199).—*Phenylhydrazine* distils without decomposition under 35 mm. pressure. It boils at 241—242° under a pressure of 750 mm. (column of mercury surrounded by vapour). At 22·7° the sp. gr. of the base is 1·097°, compared with water at 4°.

In the preparation of methylphenylhydrazine, the author finds that the reduction of the nitrosamine (Abstr., 1878, 312) may be carried out in aqueous instead of in alcoholic solution. The base boils at 131° under 35 mm. pressure, and at 227° under 745 mm. W. C. W.

Phenylhydrazine-compounds. By C. Bülow (*Annalen*, **236**, 194—197).—Malic, tartaric, and mucic acids unite with phenylhydrazine at 130°, forming diphenylhydrazides. The malic compound, $OH{\cdot}C_2H_3(CO{\cdot}N_2H_2Ph)_2$, melts at 218°, the tartaric compound, $C_2H_2(OH)_2(CO{\cdot}N_2H_2Ph)_2$, melts at 226°, and the mucic compound at 238—240°. *Phenylacetic phenylhydrazide*, $CH_2Ph{\cdot}CO{\cdot}N_2H_2Ph$, melts at 168—169°, and dissolves freely in alcohol and acetic acid. *Ethyl oxalate phenylhydrazide* crystallises in plates and melts at 119°. *Benzil phenylhydrazine*, $COPh{\cdot}CPh{:}N_2HPh$, is formed by warming equal molecular weights of benzil and phenylhydrazine. It melts at 128—129°. W. C. W.

Dicyanphenylhydrazine-compounds. By J. A. Bladin (*Ber.*, **19**, 2598—2604). — The anhydro-compound, $NPh{<}^{N{=\!=}CMe}_{C(CN){:}N}{>}$, previously obtained by the action of acetic anhydride on dicyanphenylhydrazine (Abstr., 1885, 979) can be prepared by adding the calculated quantity of pyruvic acid to an alcoholic solution of the cyano-compound and warming gently. The author regards this compound as a derivative of the hypothetical triazole, $NH{<}^{N{:}CH}_{CH{:}N}{>}$; it will therefore be *phenylmethylcyantriazole*.

The salts of the corresponding *phenylmethyltriazolecarboxylic acid*, $C_2N_3MePh{\cdot}COOH$, are described. The *copper* salt with 1½ mols. H_2O, is obtained in the form of microscopic needles; the *silver* salt with 1½ mols. H_2O does not crystallise well; and the *lead* salt with 2½ mols. H_2O forms small, white needles; all these salts are sparingly soluble, whilst those of barium and the alkalis are easily soluble in water. The *ethyl* salt, $C_2N_3MePh{\cdot}COOEt$, is a thick, bright-yellow oil, insoluble in water, but readily soluble in alcohol, ether and benzene. With hydro-

chloric acid, a *hydrochloride*, $C_2N_3MePh{\cdot}COOH,HCl$, is obtained in small, colourless tables, which are decomposed by water. The *amide*, which can be obtained by the action of hydrogen peroxide on dicyanphenylhydrazine, crystallises in small, colourless prisms, soluble in water and alcohol, less soluble in ether, and melting at 170°. The *amidoxime* is sparingly soluble in water, but more so in alcohol, and crystallises in colourless leaflets melting at 208—210°. Acids and alkalis, with the exception of ammonia, dissolve it, whilst with acetic anhydride a compound crystallising in needles and melting at 148° is obtained.

Phenylmethyltriazole, C_2N_3HMePh, obtained by heating the acid at 180°, is an oil which does not solidify at −15°. It forms a *platinochloride*, $(C_2N_3HMePh)_2,H_2PtCl_6 + H_2O$, which crystallises from alcohol in lemon-yellow tables melting at 122—124°; it is decomposed by water.

To the compound $CN_4Ph{\cdot}CN$ obtained by the action of nitrous acid on dicyanphenylhydrazine (Abstr., 1886, 146), the author gives the name *phenylcyantetrazole*, regarding it as a derivative of the hypothetical tetrazole, $N\ll^{CH{\cdot}NH}_{N=\!=N}\gg$.

W. P. W.

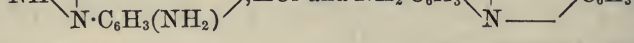
Phenazine-derivatives. By A. Bernthsen and H. Schweitzer (*Ber.*, **19**, 2604—2607).—On diazotising Witt's toluylene-red, $C_{15}H_{16}N,HCl$ (Trans., 1879, 356), a compound, *dimethamidomethylphenazine*, $NMe_2{\cdot}C_6H_3\langle^{N}_{N}\rangle C_6H_3Me$, is obtained, which forms beautiful dark-red needles or flat prisms having a greenish lustre. It dissolves in dilute acids with a violet, and in concentrated sulphuric acid with a reddish-brown coloration. Alcohol dissolves it to a red, and ether to a yellowish-red solution exhibiting golden-yellow fluorescence. It shows considerable analogy to eurhodine, and, like that base, sublimes without decomposition.

When, instead of nitrosodimethylaniline, 1:4 phenylenediamine acts on metatoluylenediamine in the presence of oxidising agents, a "simple" tolnylene-blue, and subsequently a "simple" toluylene-red are produced. On diazotising, the latter yields methylphenazine; this class of dyes must therefore be regarded as derived from phenazine. The formation of toluylene-blue is represented by the equation $NMe_2{\cdot}C_6H_4{\cdot}NH_2 + NH_2{\cdot}C_6H_3Me{\cdot}NH_2 - 4H = NMe_2{\cdot}C_6H_4\langle^{N-}_{NH}\rangle C_6H_2Me{\cdot}NH_2$. This, on further oxidation, yields toluylene-red, $NMe_2{\cdot}C_6H_3\langle^{N}_{N}\rangle C_6H_2Me{\cdot}NH_2$. The constitutional formula of the leuco-toluylene-red, $NH\ll^{-C_6H_3(NMe)-}_{C_6H_2Me(NH_2)}\gg NH$, shows a remarkable similarity to that of leucomethylene-blue. W. P. W.

Constitution of the Safranines. By A. Bernthsen (*Ber.*, **19**, 2690—2693; comp. preceding Abstract).—The fact that an indamine

is formed as an intermediate product in the preparation of phenosafranines makes it probable that the phenyl-group in the latter is combined with the same nitrogen-atom which connects the two other benzene nuclei. The constitution of leucophenosafranine (formed by oxidising equal mols. of paradiamidodiphenylamine and aniline) would thus be $NPh<^{C_6H_3(NH_2)}_{C_6H_3(NH_2)}>NH$. This reaction, and the formation of safranines by the oxidation of a paradiamine (1 mol.) with a monamine (2 mols.), explains why the para-position to the amido-nitrogen cannot be taken up, and shows that 2 atoms of nitrogen are present in safranine as amido-groups.

The following constitutional formulæ are suggested for phenosafranine hydrochloride:—



The first formula is in accordance with the analogy of the dye with the thionine-group, and the fact that rosaniline yields a triazo-derivative, although its salts contain one imido- and two amido-groups. On the other hand, the presence of two intact amido-groups in the safranine dye, and the fact that toluylene-red can also be diazotised, are in favour of the second formula (comp. also Abstr., 1885, 1026).

N. H. M.

Metanitromethylsalicylaldehyde and its Derivatives. By A. Schnell (*Chem. Centr.*, 1886, 469—470).—All attempts to prepare a hydroxymethoxybenzaldehyde by the amidation and diazotation of the above compound (first prepared by Voswinckel, Abstr., 1882, 189) were unsuccessful. An amide was formed, but was so unstable that it could not be isolated.

When metanitromethylsalicylaldehyde is heated with sodium acetate and acetic anhydride, *metanitro-orthomethoxycinnamic acid*,

$$NO_2\cdot C_6H_3(OMe)\cdot CH{:}CH\cdot COOH\ [CH : OMe : NO_2 = 1 : 2 : 5],$$

is formed. It melts at 238°, and when reduced with ammonia and ferrous sulphate yields *metamido-orthomethoxycinnamic acid*, which forms yellow needles melting at 189°. Sodium nitrite and concentrated hydrochloric acid convert this acid into *orthomethoxycinnamic acid diazochloride*, $C_6H_4(OMe)(C_3H_3O_2)\cdot N : NCl$, which is very unstable. The corresponding *nitrate* is much more stable; it explodes at 151—152°. When either of these salts is heated with water, *metahydroxyorthomethoxycinnamic acid* is formed, and yields yellow crystals melting at 179—180°. When this acid is fused with potash, it is almost completely decomposed; when methylated, it yields *methyl metorthodimethoxycinnamate* (*dimethylgentisate*), a thick, red-brown oil, which yields the *acid* on saponification. The acid melts at 143°: Tiemann and Müller (Abstr., 1882, 53) give the melting point as 76°. This

acid when oxidised with alkaline permanganate yields dimethylgentisaldehyde.

These results prove the nitro-group to be present in the meta-position. L. T. T.

New Chlorine-derivatives of Acetophenone. By H. Gautier (*Compt. rend.*, **103**, 812—814).—*Trichloracetophenone*, $COPh{\cdot}CCl_3$.—60 grams of trichloracetic chloride is mixed with 100 grams of benzene, heated to the boiling point of the latter, and aluminium chloride added in small quantities. After treatment with water, the dried product is fractionated under reduced pressure, and the portion boiling at 135—155° under a pressure of 25 mm. is re-fractionated. About 20 to 25 grams of trichloracetophenone is thus obtained as a colourless liquid with a pungent odour and extremely burning taste. It remains liquid at −21°, and boils without decomposition at 145° under a pressure of 25 mm., and with slight decomposition at 249° under atmospheric pressure; sp. gr. at 16° = 1·427. It is very slowly oxidised by alkaline potassium permanganate, yielding benzoic acid; when subjected to prolonged boiling with water, or when treated with very dilute alcoholic potash, the product is likewise benzoic acid.

Dichloracetophenone, $COPh{\cdot}CHCl_2$, is obtained in the same manner from 50 grams of dichloracetic chloride and 100 grams of benzene; the yield being about 20 grams. It is a colourless liquid, with an odour and taste resembling those of the tri-derivative. It boils unchanged at 143° under a pressure of 25 mm., and with slight decomposition at 247—248° under atmospheric pressure; sp. gr. at 15° = 1·338. It is as difficult to oxidise as the tri-derivative, and is not sensibly affected by boiling water. When subjected to prolonged treatment with an alcoholic solution of potassium acetate, the whole of the chlorine is removed with formation of potassium chloride and a product which has not yet been examined.

These derivatives afford further illustration of the stability of chlorine in combination with the carbonyl-group. It is attacked with difficulty by reagents which readily remove the chlorine from the side-chains of benzene hydrocarbons, whilst energetic reagents act on the ketonic group, and give rise to simpler substitution derivatives of benzene. C. H. B.

Action of Sulphuric Acid on Aromatic Ketones. By K. Krekeler (*Ber.*, **19**, 2623—2628; comp. Abstr., 1886, 538).—*Benzylmethylketonesulphonic acid*, $SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}COMe$, is prepared by heating benzyl methyl ketone with sulphuric acid on a water-bath. *Acetophenonesulphonic acid*, $SO_3H{\cdot}C_6H_4{\cdot}COMe$, is obtained by gradually adding pyrosulphuric acid (4 grams) to acetophenone (1 gram) kept well cooled; the intensely red liquid is then heated for half an hour on a water-bath. The *lead salt* dissolves very readily in water. The sulphonic acid reacts with phenylhydrazine, and yields the *compound* $N_2HPh : CMe{\cdot}C_6H_4{\cdot}SO_3H(N_2HPh)$; this crystallises in lustrous plates, readily soluble in alcohol.

Isobutyrothiënonesulphonic acid, $CHMe_2{\cdot}CO{\cdot}C_4SH_2{\cdot}SO_3H$, is obtained

by acting on the thiënone with pyrosulphuric acid in the cold. The *lead* and *barium salts* are very readily soluble in water, and can be crystallised from dilute alcohol. The *phenylhydrazine-derivative*, $N_2HPh : CPr^{\beta}\cdot C_4SH_2\cdot SO_3H\cdot(N_2HPh)$, crystallises in lustrous plates, readily soluble in alcohol, very sparingly in cold water.

N. H. M.

Plöchl's Phenylglycidic Acid. By E. Erlenmeyer, Jun. (*Ber.*, **19**, 2576—2577).—The phenylglycidic acid prepared by Plöchl's method (Abstr., 1884, 604) yields well characterised hydroxylamine- and phenylhydrazine-derivatives, and also gives the Laubenheimer-Victor Meyer thiophen reaction. From these facts, the author draws the conclusion that the formula $\begin{matrix}CHPh\cdot CH\cdot COOH\\ \diagdown O \diagup\end{matrix}$ suggested by Plöchl cannot be sustained, and advances the view that the compound is probably phenylpyruvic acid.

W. P. W.

Para- and Ortho-nitrophenyloxyacrylic Acid. By A. Lipp (*Ber.*, **19**, 2643—2650).—*Paranitrophenyloxyacrylic acid*, first obtained by Erlenmeyer, is readily prepared by heating paranitrophenyl-α-chlorolactic acid with alkalis; it crystallises in glistening leaflets, which melt at 186—188° with complete decomposition; when heated with sulphuric acid it yields paranitrophenylglyceric acid, which crystallises from water in small interlaced leaflets, melting at 167—168°. In order to determine whether the constitution of this acid is that of a glycide, $\begin{matrix}NO_2\cdot C_6H_4\cdot CH\cdot CH\cdot COOH\\ \diagdown O \diagup\end{matrix}$, or of a β-hydroxy-acid, its reaction with hydrochloric acid was studied; nitrophenyl-β-chlorolactic acid was formed, thus confirming the former view. This β-lactic acid resembles the corresponding α-acid in appearance and behaviour towards solvents; it forms small, glistening crystals which melt at 167—168°. When boiled with water, it is completely decomposed into hydrochloric acid, carbonic anhydride, and a red resin; its *barium* salt when heated yields paranitrophenethylaldehyde and carbonic anhydride. Since the paranitrophenyl-α- and -β-chlorolactic acids yield the same nitrophenylacrylic acid, which in its turn is reconverted into the β-lactic acid, the constitution of the oxyacrylic acid is analogous to that of glycidic acid, according to the formula written above.

The orthonitrophenylacrylic acid, obtained by Baeyer, behaves like the above in combining directly with hydrochloric and hydrobromic acids; its constitution therefore is analogous.

V. H. V.

Amido-acids. By R. Stephan (*Chem. Centr.*, 1886, 470—471).—Tiemann, Friedländer, and Priest (Abstr., 1882, 50 and 56) have shown that the cyanhydrins of aromatic aldehydes form an easy source for the preparation of substituted amido-acids. The author finds that the same holds good in the case of aldehydes of the fatty series.

Acetaldehyde cyanhydrin, when heated on the water-bath with aniline, yields *α-anilidopropionitrile*, $NHPh\cdot CHMe\cdot CN$, melting at 92°.

The *hydrochloride* forms crystals melting at 86°, and giving up hydrogen chloride very easily. The nitrile dissolves in boiling water with partial decomposition into its components. Neither hydrochloric acid nor potash causes hydrolysis, but when heated with these reagents the nitrile undergoes decomposition. When the nitrile is slowly added to concentrated sulphuric acid, *α-anilidopropionamide* is formed; this melts at 140—141°, and is decomposed when heated with strong potash. With hydrochloric acid, it yields *α-anilidopropionic acid*, which melts at 163° and sublimes unchanged.

Ortho- and para-toluidine form compounds similar to the above. *α-Paratoluidopropionitrile* melts at 82°; the *amide*,

$$C_7H_7{\cdot}NH{\cdot}CHMe{\cdot}CONH_2,$$

melts at 145°, and is more unstable than the anilido-amide; the free *acid* forms colourless, hygroscopic scales melting at 152°.

α-Orthotoluidopropionitrile melts at 72—73°, the *amide* at 125°, and the *acid* at 116° when separated from alcoholic, but at 123° from aqueous solutions.

The hydrochlorides of these nitriles yield unstable, crystalline platinochlorides.

Bromine forms tribromo-substitution products. *α-Tribromanilidopropionitrile*, $C_6H_2Br_3{\cdot}NH{\cdot}CHMe{\cdot}CN$, forms yellow needles melting at 130°; α-orthotoluidodibromopropionitrile melts at 105°, and α-paratoluidodibromopropionitrile at 117°. L. T. T.

Derivatives of Methyl Carbanilate. By W. Hentschel (*J. pr. Chem.* [2], **34**, 423—427).—In a former communication (Abstr., 1885, 792), the author has described the formation of methyl amidosulphobenzoate from methyl carbanilate by the action of sulphuric acid. When the substance is decomposed with excess of bromine-water, and the solution allowed to remain for some days, a substance of the formula $C_8H_7O_2NBr_2$ separates, which crystallises in needles, and melts at 96·5°.

This substance, in which two atoms of bromine have taken the place of the sulphonic group, when warmed with sulphuric acid yields dibromaniline sulphate, which on decomposition with sodium hydroxide gives ordinary dibromaniline (1 : 2 : 4).

When treated with nitric acid of sp. gr. 1·45, the brominated substance gives a nitro-compound, crystallising in silky needles, melting at 152°, and having the constitution

$$OMe{\cdot}CO{\cdot}NH{\cdot}C_6H_2Br_2{\cdot}NO_2 \quad [NH : Br_2 : NO_2 = 1 : 2 : 4 : 6].$$

When heated with aqueous ammonia in a sealed tube, the nitro-compound yields dibromonitraniline (m. p. 127·5°).

The acid liquid containing methyl amidosulphobenzoate yields a nitrocarbanilide when treated with strong nitric acid. This forms colourless plates or prisms, melts at 189°, and when heated with strong hydrochloric acid in sealed tubes, yields a dinitraniline which agrees in all respects with unsymmetrical metadinitraniline.

G. H. M.

Ethyl Phthalylacetoacetate. By C. Bülow (*Annalen*, **236**, 184—194).—Ethyl phthalylacetoacetate, prepared by the method described by Fischer and Koch (Abstr., 1883, 806), is decomposed by the action of sulphuric acid at 65° for half an hour, yielding alcohol and acetic and phthalylacetic acids. It is also decomposed by prolonged boiling with water or with alkalis, but with a cold alcoholic solution of potassium hydroxide it yields a deliquescent crystalline compound, $C_{14}H_{12}K_2O_6 + C_2H_6O$, which is very soluble in water. At the ordinary temperature, ammonia converts ethyl phthalylacetoacetate into phthalyldiamide, but at a temperature of 100° phthalimide is formed.

Ethyl phenylhydrazinephthalylacetoacetate, $C_{20}H_{18}N_2O_4$, forms thick plates, soluble in alcohol, in strong acetic and sulphuric acids, and in alkalis. It melts at 236—238°, and on reduction with zinc-dust and acetic acid yields the ethylic salt of benzylacetoacetic-orthocarboxylic acid. This compound melts at 92°, and dissolves freely in hot water, alcohol, ether, chloroform, and acetic acid. It is decomposed by boiling with baryta-water, yielding *benzylacetonecorthocarboxylic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COMe$. This acid dissolves freely in the usual solvents, and melts at 114°. The *phenylhydrazine* compound of *ethyl benzylacetoaceticorthocarboxylate*, $COOH\cdot C_6H_4\cdot CH_2\cdot CH(COOEt)\cdot CMe : N_2HPh$, forms pale-yellow, needle-shaped crystals. It melts with decomposition at 235°, and dissolves freely in alcohol, ether, chloroform and carbon bisulphide. At the ordinary temperature, and more rapidly at 100°, the compound splits up into alcohol, water, and a new substance, $C_{18}H_{16}N_2O_3$, which melts at 228—229°. W. C. W.

Benzoic Sulphinide. By I. Remsen and A. G. Palmer (*Amer. Chem. J.*, **8**, 223—227).—Benzoic sulphinide may be sublimed; it is decomposed by simple evaporation with strong hydrochloric acid or by boiling with strong baryta-water, yielding orthosulphobenzoic acid. The following salts are described:—$C_7H_4SO_3NK + H_2O$, very soluble crystals; $C_7H_4SO_3NAg$, sparingly soluble in boiling water, and separating in long needles; $(C_7H_4SO_3N)_2Ba + 1\frac{1}{2}H_2O$, easily soluble in water and difficult to crystallise; the methyl salt has also been prepared, but not completely examined. H. B.

Parethoxybenzoic Sulphinide. By I. Remsen and A. G. Palmer (*Amer. Chem. J.*, **8**, 227—229).—Ethoxytoluenesulphonamide (this vol., p. 136) was oxidised in warm dilute aqueous solution with potassium permanganate; from the filtered and concentrated solution, hydrochloric acid precipitated *parethoxybenzoic sulphinide*,

$$EtO\cdot C_6H_3<\begin{matrix}SO_2\\CO\end{matrix}>NH.$$

The substance forms needle-shaped crystals, melting at 257—258°; it has not a sweet taste. The potassium and silver salts, $C_9H_8SO_4NK$ and $C_9H_8SO_4NAg$, are described. H. B.

Parabromobenzoic Sulphinide. By I. Remsen and W. S. Bayley (*Amer. Chem. J.*, 8, 229—235).—Parabromotoluenesulphonamide (Hübner and Post, this Journal, 1874, 57) was oxidised with potassium permanganate in considerable excess, when besides the sulphinide, there is also formed a considerable quantity of parabromosulphobenzoic acid; this substance is not formed if potash is also added during the oxidation. *Parabromobenzoic sulphinide* is sparingly soluble in cold water, volatilises at about 200°, melts at 217°, and is characterised by an extremely sweet taste, followed by an after-taste of extreme bitterness. The following salts are described:—$(C_7H_3O_3SNBr)_2Ba + 7\frac{1}{2}H_2O$; $(C_7H_3O_3SNBr)_2Ca + 7\frac{1}{2}H_2O$; $C_7H_3O_3SNBrAg + 2\frac{1}{2}H_2O$. When treated with phosphorus pentachloride, and then with alcohol, the ethyl salt, $C_7H_3O_3SNBrEt$, is obtained as a substance which after recrystallisation from hot alcohol melts at 199—199·5°. Attempts to prepare the ethyl salt from the silver salt and ethyl iodide were unsuccessful, a mixture of at least two substances being obtained. H. B.

Benzoyltoluenesulphonamide and some of its Derivatives. By I. Remsen and C. S. Palmer (*Amer. Chem. J.*, 8, 235—243).—Somewhat similar to the sulphinides is the class of substances represented by benzoylbenzenesulphonamide, $Ph{\cdot}CO{\cdot}NH{\cdot}SO_2{\cdot}Ph$, and benzoyltoluenesulphonamide, $Ph{\cdot}CO{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$, obtained by the action of benzoic chloride on the corresponding amides. But the constitution of these substances has not been definitely proved, and Wolkow has shown that benzamide when treated with benzenesulphochloride yields not benzoylbenzenesulphonamide, but toluenesulphonic acid and phenyl cyanide, and it is, therefore, possible that the above two substances are represented, not by $R{\cdot}SO_2{\cdot}NH{\cdot}COR$, but by $R{\cdot}SO_2{\cdot}N : C(OH)R$. On the first of these suppositions, two ethyl salts should be obtained, one, $R{\cdot}SO_2{\cdot}NEt{\cdot}COR$, from the silver or lead salts and ethyl iodide, and the other, $R{\cdot}SO_2{\cdot}N : CR{\cdot}OEt$, by acting on the sulphonamide with phosphorus pentachloride and alcohol; on the second supposition, only one ethyl salt can be prepared by either method, namely, $R{\cdot}SO_2{\cdot}N : CR{\cdot}OEt$. It has already been shown, and is confirmed by the authors, that ethereal salts of benzoyltoluene-sulphonamide cannot be obtained by the action of phosphorus pentachloride and alcohol. Neither can they be obtained by the action of ethyl iodide on the lead or silver salts of the sulphonamide; similar n gative results have been recorded by other writers.

But although the ethereal salts of the sulphonamides cannot be obtained from the sulphonamides, they may nevertheless be prepared indirectly. *Benzoylmethyltoluenesulphonamide*, $C_7H_5O{\cdot}NMe{\cdot}C_7H_7SO_2$, crystallises with difficulty; it melts at 58°, and is prepared by the action of benzoic chloride on *methylparatoluenesulphonamide*, $NHMe{\cdot}SO_2{\cdot}C_7H_7$. On adding water to its alcoholic solution, the latter crystallises in plates melting at 75°, is very stable, and is obtained by treating paratoluenesulphochloride with methylamine.

Benzoylethyltoluenesulphonamide was prepared, but not analysed; it is obtained from benzoic chloride and *ethylparatoluenesulphonamide*,

$NHEt{\cdot}SO_2{\cdot}C_7H_7$, melting at 58°, and prepared like the above methyl-compound.

Benzoylphenyltoluenesulphonamide crystallises readily from alcohol; the crystals melt at 149°; when boiled with alcoholic potash, it yields benzoic acid and toluene-sulphanilide. It is prepared from *phenyl-paratoluenesulphonamide*, $NHPh{\cdot}SO_2{\cdot}C_7H_7$, melting at 103°, and already prepared by Müller. H. B.

Separation of the Two Isomeric Toluidinesulphonic Acids. By E. A. Schneider (*Amer. Chem. J.*, **8**, 274).—The potassium and sodium salts of paratoluidinemetasulphonic acid are very soluble in water, but insoluble in cold aqueous potash, whilst the potassium and sodium salts of paratoluidineorthosulphonic acid are very easily soluble in the same liquid at ordinary temperature. H. B.

Action of Concentrated Sulphuric Acid on Hydrazinetoluenesulphonic Acids. By E. A. Schneider (*Amer. Chem. J.*, **8**, 271—273).—It was hoped that condensation might be effected between the hydrazine- and sulphonic-groups. Parahydrazinetoluene-orthosulphonic acid apparently underwent no change. Parahydrazine-toluenemetasulphonic acid reacts violently with sulphuric acid at 80°; the product poured into water gives a bright red precipitate, not further examined, and the filtrate, with excess of soda, gives a yellow precipitate which resembles in all its properties the basic substance obtained by Gallinek and Richter (Abstr., 1886, 236) by heating paratolylhydrazine with sulphuric acid, and is probably identical with it. H. B.

Oxidation by Means of Potassium Permanganate. By I. Remsen and W. H. Emerson (*Amer. Chem. J.*, **8**, 262—268).—It has been stated "that acid oxidising agents tend to transform para-groups (hydrocarbon-chains) and leave ortho-groups unchanged, and that alkaline oxidising agents tend to transform ortho-groups and leave para-groups unchanged," and R. Meyer and Baur (Abstr., 1881, 46) have adduced in favour of this the case of cymenesulphonic acid [$Me : SO_3H : Pr = 1 : 2 : 4$], which with permanganate yields hydroxypropylsulphobenzoic acid [$COOH : SO_3H : C_3H_7O = 1 : 2 : 4$], but with nitric acid yields sulphoparatoluic acid [$CH_3 : SO_3H : COOH = 1 : 2 : 4$]. On the other hand, Jacobsen has shown that metaxylene-sulphonamide [$SO_3H : Me : Me = 1 : 2 : 4$] yields the same product of oxidation [$SO_3H : Me : COOH = 1 : 2 : 4$] with either chromic acid or potassium permanganate.

Jacobsen's work is fully confirmed, and it is also shown that paraxylenesulphonic acid and paraxylenesulphonamide yield the same oxidation products with permanganate, namely, sulphoterephthalic acid and a sulpho- or sulphamido-paratoluic acid. By fusing the last-named compounds with potash, they are both converted into one and the same hydroxytoluic acid, α-orthohomometahydroxybenzoic acid [$Me : OH : COOH = 1 : 2 : 4$], and hence the methyl-group first oxidised is not that which is in the ortho-position relatively to the sulphonic group.

The work of Meyer and Baur was then repeated and fully confirmed, and finally the behaviour of cymene itself with alkaline permanganate was examined. It was found that the products of the oxidation were almost equal quantities of terephthalic acid and of hydroxypropylbenzoic acid, $COOH \cdot C_6H_4 \cdot C_3H_7O$, which was recognized by converting it into propenylbenzoic acid and isopropenylbenzoic acid. Cymene treated with chromic acid yields as the first product toluic acid, and hence the cause of the different behaviour of cymenesulphonic acid towards alkaline permanganate solution, and towards acid oxidising agents (nitric acid) is not to be sought for in the influence of the sulphonic group on the hydrocarbon side-chains (Meyer), but in the difference between the side-chains themselves, the isopropyl-group yielding most easily to acid oxidising agents, the methyl-group yielding most easily to alkaline oxidising agents. (Compare Abstr., 1886, 541.) H. B.

Action of Bromine and Water on α-Metaisocymenesulphonic Acid: Constitution of α- and β-Metaisocymenesulphonic Acids. By W. Kelbe and N. v. Czarnomski (*Annalen*, **235**, 272—299).—In addition to the results which have previously appeared in this Journal (Abstr., 1882, 619; 1884, 1355; and 1886, 355), the authors describe the following compounds:—

Lead β-bromometisocymenesulphonate, $Pb(C_{10}H_{12}BrSO_3)_2 + H_2O$, crystallises in needles, and is soluble in alcohol and in hot water. The barium salt forms colourless plates; the copper salt glistening green plates containing 4 mols. H_2O; and the potassium salt, $C_{10}H_{12}Br \cdot SO_3K + H_2O$, silky needles. The sulphonamide,

$$C_{10}H_{12}Br \cdot SO_2 \cdot NH_2,$$

melts at 162° and dissolves in strong alcohol, from which solvent it is deposited in transparent needles.

α-Bromisocymenesulphonic acid is very hygroscopic. After drying over sulphuric acid, it melts at 126°. Its salts are much more soluble than those of the β-acid. The barium and copper salts crystallise with 7 mols. H_2O. The potassium salt crystallises in needles containing 1 mol. H_2O. It dissolves readily in water or alcohol. The sodium salt contains 2 mols. H_2O. The sulphonamide forms long, white, needle-shaped crystals. It melts at 170·5°, and dissolves in hot water and alcohol.

Pure α-bromisocymene, $C_{10}H_{13}Br$, boils at 225° instead of 235° as previously stated (Abstr., 1882, 618).

Dibromocymene is prepared by the action of bromine on an aqueous solution of α-bromocymenesulphonic acid. It is an oily liquid boiling at 272—273°. Pure bromocymene is obtained as a strongly refractive liquid when potassium β-bromometaisocymenesulphonate is decomposed by superheated steam. It boils at 224°, one degree lower than the α-compound, and is slowly oxidised by nitric acid, yielding bromometatoluic acid (m. p. 152°), $C_6H_3MeBr \cdot COOH$ [1 : 4 : 3].

General Conclusions.—When metaisocymene dissolves in sulphuric acid, the SO_3H group displaces the H atoms at 4 or 6. Bromine

displaces the H atom at 4 in α-cymenesulphonic acid, and at 6 in the β-acid.

When bromocymenes are dissolved in sulphuric acid, the sulphonic group takes the position 4 in the α-compound, and 6 in the β-compound. The constitution of these compounds is shown in the following table :—

	α.	β.
Bromotoluic acids, Me : COOH : Br	1 : 3 : 6	1 : 3 : 4
Bromocymene, Me : Pr : Br	1 : 3 : 6	1 : 3 : 4
Cymenesulphonic acid, Me : Pr : SO_3H ..	1 : 3 : 6	1 : 3 : 4
Bromocymenesulphonic acid, Me : Pr : SO_3H : Br.....	1 : 3 : 4 : 6	1 : 3 : 6 : 4
Dibromocymene, Me : Pr : Br : Br	1 : 3 : 4 : 6	
Bromoisophthalic acid, COOH : COOH : Br	1 : 3 : 6	1 : 3 : 4

W. C. W.

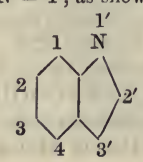
Synthesis of Indole-derivatives. By E. Fischer (*Annalen*, **236**, 116—126).—Many of the results contained in this paper have already been published (Abstr., 1884, 52, 1180; and 1886, 835).—The fæcal odour of indole is most marked in skatole, and in the mono- and di-methyl compounds with the exception of those substances in which the methyl-group is united to the N-atom. The odour and volatility of the compounds is destroyed by the introduction of the phenyl-group. All indole-derivatives form crystalline picrates, and all the indoles with the exception of the carboxylic acids are reduced by zinc and hydrochloric acid to hydro-bases. The pine-wood reaction is not exhibited by the carboxylic acids, nor by those derivatives in which both the 2′ and 3′* hydrogen-atoms are replaced by methyl, ethyl, &c.

Nitrous acid converts indole and 1′ methylindole into nitroso-compounds. It forms complicated products with 2′ methyl or phenyl indole, and converts 3′ or 2′, 3′ substituted indoles into nitrosamines.

The following is a list of indoles derived from the hydrazines.

		Melting point.	Boiling point.
Monomethyl	1′.....	liquid	240°
	2′.....	60°	272
	3′.....	95	265–266
Dimethyl ..	2′ : 3′	106	285
	1′ : 2′	56	?
	1 : 3′	liquid	?
	3 : 1′	„	?
	1 : 1′	„	?

* *Note.*—In the notation of the indole series, 1, 2, 3, 4 refer to the positions in the benzene-ring, and 1′, 2′, 3′ to the corresponding positions in the basic ring containing the nitrogen, where N = 1′, as shown in the annexed symbol :—



—Editors.

		Melting point.	Boiling point.	
Trimethyl..	1′ : 2′ 3′	liquid	?	picrate melts at 150°.
Ethyl	1′.....	,,		
Methyl ethyl	2′ : 3′	,,	291—293°	
	3 : 1′	,,	?	
Monophenyl	1′	,,		
	2′	186°		
Diphenyl...	2′ : 3′	123		
Benzyl	1′.....	44·5°		
Naphthindole	2′.....	liquid	222° under 18 mm. pressure.	
Methyl naphthindole, 2′ ..		,,		

W. C. W.

Indoles from Phenylhydrazine. By E. Fischer (*Annalen*, **236**, 126—151).—Most of the compounds mentioned in this paper have already been described by the author (Abstr., 1886, 805). 2′, 3′ *Dimethylindole*, $C_8NH_5Me_2$, prepared from the phenylhydrazine compound of methyl ethyl ketone, melts at 106° and boils at 285°. The nitrosamine, $C_8NH_4Me_2{\cdot}NO$ [NO = 1′], melts at 61—62°, and decomposes at a higher temperature. 2′ 3′ *Methylethylindole*, C_8NH_5MeEt, prepared from the phenylhydrazine of methyl propyl ketone, is an oily liquid boiling at 291—293°. The picrate crystallises in dark red needles. Phenylhydrazinelævulinic acid,

$$PhN_2H : CMe{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

melts at 108°, and at a higher temperature splits up into water and the anyhdride, $C_{11}H_{12}N_2O$. This substance crystallises in colourless plates. It melts at 106—107° and boils between 340° and 350° with partial decomposition. Ethyl phenylhydrazinelævulinate melts at 110°. *Methylindoleacetic acid*, prepared from this ethyl salt, melts between 195° and 200°, and splits up into carbonic anhydride and 2′, 3′ dimethylindole. W. C. W.

Indoles from Methylphenylhydrazine. By J. Degen (*Annalen*, **236**, 151—164).—The preparation of 1′, 2′ dimethylindole, 1′, 2′ methylphenylindole, and 1′, 2′, 3′ dimethylindolecarboxylic acid from the compounds of methylphenylhydrazine with acetone, acetophenone, and ethyl acetoacetate, respectively, has already been described (Abstr., 1886, 805). Dimethylindolecarboxylic acid crystallises in six-sided plates. It melts at 185° with partial decomposition into carbonic anhydride and 1′, 2′ dimethylindole. 1′, 2′, 3′ Dimethylindoleacetic acid (*loc. cit.*) melts at 188° and decomposes at 200°, yielding 1′, 2′, 3′ *trimethylindole*, an oily liquid which boils about 280° without decomposition. The picrate melts at 150°. Trimethylindole is obtained in a less pure state by the action of zinc chloride on the compound of methylphenylhydrazine with methyl ethyl ketone. 1′, 3′ Dimethylindole is obtained in an impure state by acting on propylidenemethylphenylhydrazine with zinc chloride.

W. C. W.

Indoles from Metahydrazinebenzoic Acid. By A. Roder (*Annalen*, **236**, 164—173). — Metahydrazinebenzoic acid is con-

veniently prepared by adding the theoretical quantity of sodium nitrite to 100 grams of metamidobenzoic acid suspended in a mixture of 400 grams of water and 190 grams of strong hydrochloric acid. The liquid is poured into an ice-cold solution of sodium sulphite (4 mols. Na_2SO_3 to 1 mol. amido-acid). As soon as the mixture turns yellow, strong hydrochloric acid is added to precipitate the hydrochloride of metahydrazinebenzoic acid. The free acid is obtained by adding sodium acetate to a solution of the hydrochloride. The acetone compound is formed when acetone and sodium acetate or potassium hydroxide are added to a solution of the hydrochloride. This substance forms colourless needles melting at 150°. It is freely soluble in alcohol and acetic acid, and is easily decomposed by warm mineral acids into acetone and hydrazinebenzoic acid. The *ethylic* salt $C_{10}H_{11}N_2O_2Et$, melts at 90—91° and dissolves freely in alcohol, ether and acetic acid. *Hydrazinebenzopyruvic acid*, $C_{10}H_{10}N_2O_4 + H_2O$, melts at 206—208° with decomposition, and is freely soluble in ammonia and fixed alkalis. The barium and sodium salts are crystalline. The *ethyl* salt, $C_{10}H_8N_2O_4Et_2$, melts at 101—102°. It dissolves freely in alcohol, ether, and in warm benzene. By the action of zinc chloride on this compound, the ethyl salt of indoledicarboxylic acid is formed, together with indole and a small quantity of another substance. *Monethyl indoledicarboxylate* crystallises in needles and melts at 250° with decomposition. It is freely soluble in alcohol. The free acid melts at 250° with decomposition. It dissolves freely in hot alcohol and in acetic acid. It has the constitution $[(COOH)_2 = 4:2'$ or $3:2']$. Hydrazinebenzoic acid unites with benzaldehyde, forming *benzylidenehydrazinebenzoic acid.* This acid crystallises in plates, melts at 170—172°, and is freely soluble in alcohol and acetic acid. *Phenylglucosazonecarboxylic acid* melts at 206—208° with decomposition. Metahydrazinebenzoic acid unites with phenyl isothiocyanate, forming *diphenylthiosemicarbazidecarboxylic acid*, $C_{14}H_{13}N_3O_2$. This substance crystallises in colourless needles and melts at 204—205° with decomposition. W. C. W.

Aluminium Chloride Reaction. By R. Anschütz (*Annalen*, **235**, 150—229 and 299—341). The experimental results of the author's research on the aluminium chloride reactions have already been published (Abstr., 1883, 807, 809, 1132; 1884, 326, 753, 754, 1034; 1885, 269, 768, 769). The following conclusions are deduced from these results.

Dibenzyl and unsymmetrical diphenylethane (obtained by the action of aluminium chloride and benzene on the isomeric dibromethylenes) correspond with the dibromethylenes in constitution.

The synthesis of anthracene from aluminium chloride, benzene, and acetylene tetrabromide, indicates that the mesocarbon-atoms in anthracene are probably linked together. The formation of dimethylanthracene from toluene, acetylene tetrabromide, and aluminium chloride, shows that the methyl-groups in dimethylanthracene, melting at 225°, are divided between the two benzene nuclei. Aluminium chloride not only removes but also transfers the side-chains of methyl-

and ethyl-benzenes from one molecule to another. Only the symmetrical tetraphenylethane is known.

In many aluminium chloride reactions, theoretical yields are obtained when carbon bisulphide is used as a diluent.

Symmetrical mesodimethylanthracene hydride is formed, together with ethylbenzene and unsymmetrical diphenylethane, by the action of benzene and aluminium chloride on ethylidene bromide or chloride, or on vinyl bromide. Ethyltoluene, unsymmetrical ditolylethane, and tetramethylanthracene hydride are formed by the action of aluminium chloride on ethylidene chloride and toluene. A new dimethylanthracene is formed by heating the tetramethylanthracene hydride with zinc-dust. W. C. W.

Dehydrogenation by Means of Benzoic Peroxide. By E. Lippmann (*Monatsh. Chem.*, **7**, 521—528).—Benzoic peroxide can react as a dehydrogenising agent, removing two hydrogen-atoms from two molecules of an aromatic hydrocarbon. Thus from toluene a hydrocarbon, $C_{14}H_{12}$, is formed; the hydrocarbon boils at 258—262°, is strongly refractive, and of aromatic odour, sp. gr. 1·0032; it is isomeric with stilbene and diphenylethylene, and as, on oxidation, it yields benzoic acid only, its constitution is probably expressed by the formula $<^{C_7H_6}_{C_6H_4}>CH_2$, that of a benzylidenetolylene.

Similarly from xylene, a hydrocarbon, $C_{16}H_{16}$, is obtained as a refractive liquid, boiling at 260—270°, sp. gr. 998; as being isomeric with ditolylethylene and dimethylstillene, it is named dixylylene. V. H. V.

Formation of Substituted Stilbenes. By K. Elbs (*J. pr. Chem.* [2], **34**, 340—342).—On endeavouring to extend Strakosch's method of synthesis of stilbene-derivatives by the action of potash on benzyl-derivatives, the reaction with orthonitrobenzyl chloride was successful, but in the case of parabromobenzyl bromide the corresponding alcohol was obtained together with ethyl parabromobenzoate; the latter substance, the derivation of which in the above reaction is not satisfactorily explained, is a colourless viscid liquid, boiling at 236° under a pressure of 713 mm., of odour resembling pears, soluble in most menstrua with the exception of water, saponified only with difficulty. V. H. V.

Substituted Stilbenes. By K. Elbs and F. Bauer (*J. pr. Chem.* [2], **34**, 343—347).—Paradinitrostilbene is not altered by potassium permanganate; on oxidation with chromic acid in acetic acid solution, it is readily converted into paranitrobenzoic acid. With bromine, it forms *paradinitrostilbene bromide*, $NO_2{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4{\cdot}NO_2$, a white, crystalline powder melting above 300°, but decomposing even at 110° with evolution of hydrobromic acid and the formation of paradinitrotolane; it is sparingly soluble in most menstrua. When an acetic acid solution of paradinitrostilbene bromide is boiled with potassium acetate, ethyl paradinitrohydrobenzoin acetate,

$$NO_2{\cdot}C_6H_4{\cdot}CH(OAc){\cdot}CH(OAc){\cdot}C_6H_4{\cdot}NO_2,$$

is formed; this crystallises in small, yellow crystals, melting at 340°, moderately soluble in alcohol, ether, and acetic acid.

Paradinitrotolane, $NO_2 \cdot C_6H_4 \cdot C : C \cdot C_6H_4 \cdot NO_2$, obtained as described above, and best purified by sublimation, crystallises in needles melting at 288°; it usually separates from solvents in the amorphous form.

V. H. V.

Euxanthone-group. By C. Graebe and A. Feer (*Ber.*, **19**, 2607—2614).—Spiegler (Abstr., 1884, 1182) ascribed to benzophenone oxide the constitution $<\begin{matrix}C_6H_4 \cdot O-\\ C_6H_4 \cdot CO\end{matrix}>$, as it reacts neither with hydroxylamine nor with phenylhydrazine. The authors suggest for this compound the constitution $C_6H_4<\begin{matrix}O\\ \diagup\diagdown\\ C\end{matrix}>C_6H_4$; this would account for the negative result with hydroxylamine, as well as for the fact that it yields dihydroxybenzophenone when fused with potash (Richter, Abstr., 1884, 324).

Orthodihydroxybenzophenone (Richter, *loc. cit.*) boils at 330—334° with partial decomposition into water and benzophenone oxide. The potassium salt has the formula $CO(C_6H_4 \cdot OK)_2$. The *phenylhydrazine* and *hydroxylamine-compounds* melt at 152° and 99° respectively. The methyl salt was found to melt at 104° (not 98°); it undergoes no change when heated with alcoholic potash at 150°; the *hydroxylamine-derivative* melts at 188°. The *ethyl salt* crystallises from alcohol in colourless needles melting at 109°; the *phenylhydrazine-compound* melts at 114°. The acetyl-derivative melts at 96° (not 83°). When paracresol salicylate is subjected to the same treatment as the phenyl salt in the preparation of benzophenone oxide (Siefert, Abstr., 1885, 1058), the *compound* $C_6H_4<\begin{matrix}CO\\ -O-\end{matrix}>C_6H_3Me$ is formed; this is very readily soluble in hot alcohol and melts at 105°. α-Naphthol salicylate yielded *α-naphthophenone oxide*, $C_{17}H_{10}O_2$; it melts at 155°, and dissolves very readily in hot toluene. The *picrate* is yellowish-red. *β-Naphthophenone oxide* crystallises in needles melting at 140°.

When euxanthonic acid is fused with potash, it is converted into quinol; it has therefore the constitution

$$C_6H_3(OH)_2 \cdot CO \cdot C_6H_3(OH)_2 \; [CO : OH : OH = 6 : 1 : 4].$$

An *ethyl salt* was obtained which reacts with hydroxylamine.

N. H. M.

Preparation of Dinitronaphthylamine: Metanitrophenylazodimethylamidobenzene. By R. Meldola (*Ber.*, **19**, 2683—2684).—α-Naphthylamine is boiled for several hours with acetic acid; the theoretical amount of nitric acid (sp. gr. 1·5) diluted with glacial acetic acid is then gradually added to the warm solution of the acetonaphthalide and the whole warmed until the reaction is finished. The product is then poured into cold water, filtered, and washed well with cold water. The precipitate whilst still moist, is mixed in small quantities with strong sulphuric acid and warmed; it is then poured into cold water, and the orange-red precipitate washed with water; it may be purified by recrystallisation from alcohol. The yield of crude substance is almost theoretical.

Metanitrophenylazodimethylamidobenzene (Staedel and Bauer, Abstr., 1886, 944) has already been fully described by the author (Trans., 1884, 120). N. H. M.

Eurhodines and Laurent's Naphthase. By O. N. Witt (*Ber.*, **19**, 2791—2796).—The *eurhodol*, $C_{14}H_8 \begin{array}{l}\diagup N \\ \diagdown N\end{array} C_{10}H_5 \cdot OH$, is obtained by fusing sodium diphenylenenaphthaquinoxalinesulphonate (Abstr., 1886, 889) with potash until the yellow colour suddenly changes to a pure cinnabar-red. When the product is diluted with water and treated with hydrochloric acid in excess, the *hydrochloride* separates as a cinnabar-red, insoluble powder. If acetic acid is used in the place of hydrochloric acid, the free eurhodol separates in orange-yellow crystalline flakes. It is insoluble in all solvents and can only be purified by recrystallising the hydrochloride from boiling phenol. When heated, it sublimes with partial decomposition. Sulphuric acid dissolves it with a pure deep blue colour which changes immediately on addition of very little water to a splendid carmine-red; when the blue solution is heated to a certain point it becomes successively violet, red, and yellow. The dry eurhodol is electric.

α-β-Naphthaquinoxaline, $C_{10}H_6 \begin{array}{l}\diagup N \\ \diagdown N\end{array} C_{10}H_6$, is prepared by the action of β-naphthaquinone on orthonaphthylenediamine in acetic acid solution; it is purified by crystallisation from naphthalene. It forms yellow needles melting sharply at 275°. It dissolves in sulphuric acid, yielding a pure violet solution which becomes orange-yellow when diluted; when further diluted, the free base is precipitated. It sublimes readily in long, yellow needles, and when quickly heated distils as a yellow oil which soon solidifies. It is identical with Laurent's naphthase (*Annalen*, **9**, 384; compare also Nietzki and Goll, Abstr., 1885, 545). N. H. M.

Indoles from β-Naphthylhydrazine. By A. Schlieper (*Annalen*, **236**, 174—184).—The β-naphthylhydrazine described by E. Fischer (Abstr., 1886, 555) unites with acetone, forming the compound $C_{10}H_7 \cdot N_2H : CMe_2$. This substance crystallises in prisms of a pale-yellow colour. It melts at 65·5°, and is freely soluble in alcohol, ether, benzene, acetone, and in (hot) light petroleum. *Ethylidene β-naphthylhydrazine*, $C_{10}H_7 \cdot N_2H : CHMe$, forms three-cornered plates, soluble in hot alcohol, benzene, and chloroform. It melts at 128—129°. *β-Naphthylhydrazinepyruvic acid*, $C_{10}H_7 \cdot N_2H : CMe \cdot COOH$, forms yellow needles. This acid melts at 166°, and decomposes with evolution of carbonic anhydride. It dissolves in hot alcohol and acetic acid. The ethyl salt melts at 131°, and is freely soluble in alcohol, ether, benzene, and acetic acid. On fusion with zinc chloride, β-naphthindole is produced; β-naphthindolecarboxylic acid is formed as an intermediate product. After purification by conversion into the picrate, β-naphthindole, $C_{10}H_6 \begin{array}{l}\diagup NH \\ \diagdown CH\end{array} \rangle CH$, boils at 222° under 18 mm. pres-

sure, and above 360° under the ordinary atmospheric pressure. It dissolves in alcohol, ether, benzene, and acetic acid with fluorescence. Strong hydrochloric acid forms a crystalline compound with it.

β-Naphthindolecarboxylic acid, $C_{10}H_6<\begin{matrix}NH\\CH\end{matrix}>C\cdot COOH$, crystallises in colourless plates, soluble in alcohol and acetic acid. It melts at 226° with evolution of carbonic anhydride. The sodium and barium salts are sparingly soluble in cold water. The ammonium and potassium salts are much more soluble.

Methylnaphthindole, $C_{10}H_6<\begin{matrix}NH\\CH\end{matrix}>CMe$, from acetone-β-naphthylhydrazine, boils between 314° and 320° under a pressure of 223 mm. It is freely soluble in alcohol, ether, and benzene. The picrate melts at 176°. On reduction with nascent hydrogen, *hydromethyl-β-naphthindole* is obtained as an oily liquid, boiling between 190 and 200° under 20 mm. pressure. It is a strong base, and with mineral acids, forms salts which are very soluble in water. W. C. W.

Action of Monamines on Citric Acid. By H. Hecht (*Ber.*, **19**, 2614—2618).—*Citrotrimethylamide*, $C_6H_5O_4(NHMe)_3$, is prepared by adding a strong solution of methylamine to a concentrated solution of methyl citrate in absolute alcohol, and keeping the product over sulphuric acid for some time. It separates in prisms melting at 124°; it is very readily soluble in cold water, and is not acted on by alkali or hydrochloric acid.

Citrodinaphthylamide, $C_{10}H_7\cdot N : C_6H_5O_4\cdot NH\cdot C_{10}H_7$, is formed when a mixture of citric acid (1 mol.) and β-naphthylamine (3 mols.) is heated at 140—150° for several hours. It crystallises in six-sided plates melting at 233°. It is insoluble in water or hydrochloric acid, sparingly soluble in alcohol.

The *trinaphthylamide*, $C_6H_5O_4(NH\cdot C_{10}H_7)_3$, is obtained by heating the dinaphthylamide with naphthylamine (eq. mols.) at 150—160°; it forms microscopic, prismatic crystals readily soluble in alcohol, insoluble in water; it melts at 215°, and is very stable.

Citrodinaphthylamic acid, $OH\cdot C_6H_5O_4(NH\cdot C_{10}H_7)_2$, is prepared by heating the dinaphthylamide with an excess of concentrated ammonia for six hours at 170°. It crystallises from alcohol in slender, microscopic needles melting at 172°; it is readily soluble in alkali, insoluble in water. The *silver salt* was prepared.

Monobasic naphthylamine citrate, $C_6H_8O_8,NC_{10}H_9$, separates as a rose-coloured substance when a hot, concentrated alcoholic, solution of citric acid (1 mol.) is mixed with β-naphthylamine (1 mol.) and cooled. It melts at 89°, dissolves readily in alcohol, ether, nitrobenzene, and water.

Compounds isomeric with the above were prepared from α-naphthylamine in a similar manner. *Citrodinaphthylamide* is purified by precipitating the solution in glacial acetic acid with water; it crystallises from benzene in six-sided plates melting at 194°; it is insoluble in hydrochloric acid. *Citrotrinaphthylamide*, $C_6H_5O_4(NHC_{10}H_7)_3$, crystallises in microscopic, rhombic prisms which melt at 129°. Boiling alkali solution and acids do not act on it. *Citrodinaphthylaminic acid*

crystallises in small groups of needles melting at 149°; the alcoholic solution reacts slightly acid. The *silver salt* is sparingly soluble in water. N. H. M.

Action of Ammonia on Ethyl Acetonedicarboxylate: Synthesis of Pyridine-derivatives. By H. N. Stokes and H. v. Pechmann (*Ber.*, **19**, 2694—2717).—Ethyl β-hydroxamidoglutamate (Abstr., 1885, 1202) is readily soluble in hot water and in alcohol; the aqueous solution decomposes gradually, giving off ammonia. It gives a deep red coloration with ferric chloride.

The compound obtained by the action of alkalis on ethyl β-hydroxamidoglutamate and described as glutazine (*loc. cit.*), is shown to be a pyridine-derivative, probably having the constitution

$$NH<\begin{matrix}CO\cdot CH_2\\CO\cdot CH_2\end{matrix}>C:NH.$$

It melts at about 300° with evolution of ammonia, is moderately soluble in hot water, almost insoluble in hot alcohol, and insoluble in other solvents. The neutral solution acquires a deep-red colour on addition of ferric chloride; on warming, the solution turns dark-green without becoming turbid. The *hydrochloride* (with 1 mol. H_2O) crystallises in prisms readily soluble in alcohol; water decomposes it. The *sulphate* was prepared. The *sodium*, *ammonium*, and *barium salts* are very soluble.

Pentabromacetylacetamide (*loc. cit.*) melts at 148°; at a higher temperature, it gives off bromine and hydrogen bromide. It is insoluble in water, readily soluble in alcohol, ether and glacial acetic acid, moderately in chloroform. When heated with water, it is converted into dibromacetamide, bromoform, and carbonic anhydride. Boiling alcoholic ammonia converts it into dibromomalonamide (melting at 200·5°) and bromoform.

Acetylglutazine, $NH<\begin{matrix}CO\cdot CH_2\\CO\cdot CH_2\end{matrix}>C:NAc$, is obtained by heating glutazine with acetic chloride at 100—120°. It crystallises from water in small lustrous plates, which darken at 230° and melt at 285—290°. When warmed with ferric chloride, it acquires a brilliant violet colour. The *ammonium* (with 1 mol. H_2O), *silver*, and *barium salts* were prepared.

2, 4, 6 *Trihydroxypyridine* is prepared by boiling glutazine for 3—4 minutes with an excess of strong hydrochloric acid and then evaporating the solution in clock glasses as quickly as possible on a water-bath. The dry residue is extracted with cold alcohol and the solution quickly evaporated; the thick syrup so formed is mixed with a little water and a solution of caustic soda (0·3 gram to 1 gram glutazine) in twice its weight of water added, the whole being kept cool. The crystalline product is washed with a little water and dried. It forms yellow, microscopic needles which swell up when heated at 220—230° and give off water. It dissolves readily in hot water, but is insoluble in other solvents. When treated with ferric chloride, it gives a deep-red coloration. Bromine-water converts it into pentabromacetylacetamide. It reacts strongly acid and decomposes carbonates. The salts

of the alkalis and alkaline earths are very readily soluble in water. When distilled with zinc-dust, it yields a small quantity of pyridine. Hydroxylamine hydrochloride reacts with trihydoxypyridine, yielding a *monoxime*, $C_5NH_3O_2 : N{\cdot}OH + H_2O$. The latter is a heavy, sandy powder consisting of hexagonal plates; it melts at 194—196° with evolution of gas. It is rather soluble in hot water, less so in alcohol. When treated with strong soda solution, it becomes blue; with ammonia, it gives a yellowish-red colour which changes to intense purple when warmed. The oxime forms salts with acids. It is also formed by acting on glutazine with hydroxylamine. The *phenylhydrazine-compound* (obtained from both trihydroxypyridine and glutazine) forms plates readily soluble in hot alcohol; it melts at 230°.

When trihydroxypyridine is heated with ammonium acetate at 120—140°, it is converted quantitatively into glutazine.

Trihydroxypyridine anhydride, $C_{10}H_8O_5N_2$, is formed as the chief product in the decomposition of glutazine by boiling dilute sulphuric acid. It crystallises in flesh-coloured, microscopic prisms; it is very stable, and melts only at a high temperature. It is insoluble in all neutral solvents except water, which dissolves it slowly. It dissolves readily in an excess of alkali. The *hydrogen barium salt*,

$$(C_{10}H_7O_5N_2)_2Ba + 4H_2O,$$

forms yellow prisms insoluble in water and alcohol. The normal alkali and alkaline earth salts are readily soluble in water; they are not decomposed by carbonic anhydride. The *hydrochloride* crystallises in needles readily soluble in alcohol; it is decomposed by water. The *sulphate* crystallises from water in prisms. The anhydride can be converted into trihydroxypyridine by evaporating its aqueous solution.

The way in which glutazine is formed shows that the nitrogen of the pyridine-ring has the para-position to the side-chain containing nitrogen, and the ortho-position to both the oxygen-atoms. Hence the three oxygen-atoms in trihydroxypyridine must be symmetrical to one another and to the nitrogen, and trihydroxypyridine is therefore analogous to phloroglucinol. The analogy of the two compounds is seen in their yielding anhydrides and in their behaviour towards ammonia and hydroxylamine (compare Baeyer, Abstr., 1886, 350). It is probable that the pyridine-derivative exists in two forms, as shown in the following formulæ:—

$$NH\!<\!\begin{matrix}CO{\cdot}CH_2\\CO{\cdot}CH_2\end{matrix}\!>\!CO \quad \text{and} \quad N\!\leqslant\!\begin{matrix}C(OH) : CH\\C(OH) : CH\end{matrix}\!\geqslant\!C{\cdot}OH.$$

3, 5 Dichloro-2, 6-dihydroxy-4-amidopyridine (*loc. cit.*) forms short flat needles melting at 241·5°; it dissolves sparingly in hot water and alcohol, readily in alkali and dilute hydrochloric acid.

2, 4, 6 Trichloro-4-amidopyridine forms long colourless needles melting at 157·5°; it is very readily soluble in alcohol, readily in dilute hydrochloric acid, and insoluble in alkali; it sublimes unchanged.

2, 3, 5 Trichloro-6-hydroxy-4-amidopyridine, melting at 282°, is very readily soluble in hot water, moderately in hot alcohol, sparingly in

ether and benzene. It is a monobasic acid, and decomposes carbonates. The *sodium salt* is rather soluble in water, sparingly in alcohol.

2, 3, 5, 6 Tetrachloro-4-amidopyridine melts at 212°, and sublimes unchanged. It is insoluble in water, soluble in alcohol and benzene. It can be boiled with strong sulphuric acid without decomposition. When heated with fuming hydriodic acid at 200°, black crystals of an *iodine-derivative* melting below 80° are formed. This, by solution in dilute sulphuric acid and precipitation with alkali, is converted into what is probably *dichloramidopyridine;* it melts at 158°. When the tetrachloro-compound is boiled with sodium ethoxide and alcohol, 2, 3, 5 *trichloro-6-ethoxy-4-amidopyridine* is formed; this crystallises in needles which melt at 83°. It distils with steam, is insoluble in water, alkali, and dilute acids, very readily soluble in alcohol, ether, benzene, &c. Dilute hydrochloric acid converts it (at rather above 100°) into trichlorhydroxyamidopyridine (m.p. 282°) and ethyl chloride. *Dichloro-diethoxy-3-amidopyridine*, $C_5N_2H_2Cl_2(OEt)_2$, and *dichloro-2-hydroxyethoxy-4-amidopyridine*, $C_5N_2H_2Cl_2(OH)\cdot OEt$, are formed by heating tetrachloramidopyridine with excess of sodium ethoxide and alcohol at 190°. The former crystallises in long needles melting at 98°; it is very readily soluble in alcohol and ether, insoluble in water, alkalis, and dilute acids, and distils with steam. The latter crystallises from very dilute alcohol in flat needles which melt at 161·5°. It dissolves readily in alcohol, ether and alkalis, and is insoluble in dilute acids. The two compounds are also formed from trichlorhydroxyamidopyridine and from the diethoxy-compound by the action of sodium ethoxide and alcohol at 190°. N. H. M.

Correction. By A. Ladenburg and C. F. Roth (*Ber.*, **19**, 2586; compare Abstr., 1885, 994).—The authors state that in the mixture of bases of high boiling point from animal oil examined by them, aniline was present and accumulated in the fraction 174—176°, from which they separated the supposed new lutidine. A repetition of the experiments has not yet been possible owing to a difficulty in obtaining the material. W. P. W.

Derivatives of Picolinic and Nicotinic Acids. By E. Seyferth (*J. pr. Chem.* [2], **34**, 241—263).—At the outset, unsuccessful experiments are described, made with a view of obtaining hexahydropicolinic acid from the acid itself by the action of various hydrogenising agents. But in each case either the acid was not acted on or was decomposed with formation of picoline and its hydro-derivatives.

Chloropicolinic acid, $C_5NH_3Cl\cdot COOH$, is obtained by boiling chloropicoline trichloride, $C_5NH_4Cl\cdot CCl_3$ (from picolinic acid and phosphoric chloride), with 80 per cent. sulphuric acid, and pouring the product into water. It crystallises in needles and prisms, often showing twinning. It melts at 180°, is sparingly soluble in cold water, readily soluble in hot water, alcohol and chloroform. It has strongly acid properties and does not form salts with dilute mineral acids. Its *calcium* salt crystallises with $1H_2O$ in transparent prisms, and its *barium* salt in nodular aggregates. Both salts are sparingly

soluble in cold, but readily in hot water; its *silver* salt is a voluminous, flocculent precipitate. With reducing agents, it yields picoline and picolinic acid.

Chlorohydroxypicolinic acid, $OH{\cdot}C_5NH_2Cl{\cdot}COOH$, formed simultaneously with the above, crystallises in clusters of needles, melts above 315°, is sparingly soluble in cold, readily in hot water, alcohol, and ether. Like the above acid, it does not combine with mineral acids.

These acids are not identical with those obtained by Ost (Abstr., 1883, 794). With phosphoric chloride, nicotinic acid yields an oil containing chlorine, and this, when boiled with sulphuric acid, is converted into chlorhydroxy- and dichloro-nicotinic acids, together with trichloropyridine. The first of these acids crystallises in monoclinic prisms and needles, melting at 302°, sparingly soluble in cold, readily in hot water and alcohol. The aqueous solution gives with silver nitrate a white, flocculent precipitate, soluble in ammonia, and with ferric chloride a dirty red precipitate. Its barium salt crystallises in transparent rhombic prisms.

Trichloropyridine, $C_5NH_2Cl_3$, crystallises in colourless needles, melting at 64°, insoluble in water, soluble in alcohol, ether and benzene.

Dichloronicotinic acid crystallises in small, white, grouped needles, melting at 138°; its *ethyl* salt forms colourless needles, melting at 50°, sparingly soluble in water, but soluble in alcohol, ether, and chloroform. V. H. V.

Bromoquinoline. By A. Claus and F. Collischonn (*Ber.*, **19**, 2763—2769).—It was previously mentioned (this vol., p. 60) that when quinolinepropiobromide dibromide is heated, the hydrobromide of a new monobromoquinoline is formed. The bromo-compound is heated at 170° for some time, and then at 190°; a crystalline residue is thus obtained without carbonisation. The bromoquinoline is separated from the quinoline that may be present by distilling with steam: the hydrobromide of the bromo-compound is decomposed, the free base going over with the steam, whilst the quinoline salt remains behind. It is a slightly yellow oil, having an odour resembling that of quinoline; it boils at 273—274° (uncorr.). The *hydrobromide* forms characteristic envelope-shaped crystals, which dissolve sparingly in cold water with partial decomposition, more readily in alcohol, and is almost insoluble in chloroform. When carefully heated at about 190°, it sublimes without having melted. The *hydrochloride* sublimes readily without melting. The *platinochloride*, $(C_9NH_6Br)_2,H_2PtCl_6$, crystallises from dilute hydrochloric acid in slender, orange-coloured needles. The *nitrate* and *sulphate* melt respectively at 180° and 182—183° (uncorr.). The *dichromate* crystallises in flat, short prisms, which melt at 144—145° with decomposition. The *compound* $(C_9NHBr)_2,AgNO_3$ melts at 172—173°, and detonates at a high temperature with evolution of red vapour. The same bromoquinoline is obtained when an ethereal solution of bromine is added to a solution of quinoline in ordinary ether (containing alcohol); a yellow precipitate is formed. The latter crystallises from chloroform in lustrous, garnet-coloured crystals, melting at 88° (uncorr.). Analysis points to the formula C_9NH_7,HBr,Br_2. When exposed to air it gives off bromine. The *hydrochloride*,

C_9H_7,HCl,Br_2, forms small, orange-coloured crystals melting at 100—105°. When the hydrobromide of the quinoline dibromide is heated at 180°, it is converted with evolution of hydrobromic acid into bromoquinoline hydrobromide.

When bromoquinoline is oxidised with potassium permanganate, Friedländer and Ostermayer's oxalylanthranilic acid (Abstr., 1882, 732), melting at 210° (not 200°), and *bromopyridinedicarboxylic acid*, $C_5NH_2Br(COOH)_2$, are obtained. The latter forms yellowish crystals, readily soluble in water, alcohol, ether, &c.; it melts at 165° with evolution of carbonic anhydride and formation of *bromonicotinic acid*, melting at 183° (uncorr.).

The bromoquinoline described above is identical with that obtained by La Coste (Abstr., 1881, 741) by brominating quinoline hydrochloride. N. H. M.

Synthetical Experiments with Ethyl Acetoacetate. By L. Knorr (*Annalen*, **236**, 69—115).—The action of ethyl acetoacetate on aniline at different temperatures has already been investigated by the author (Abstr., 1884, 334). The anilide of acetoacetic acid, previously described as β-phenylamido-α-crotonic acid, melts at 85° and decomposes on distillation, yielding symmetrical diphenylcarbamide. On the addition of bromine to a solution of the anilide in chloroform, an unstable additive product is formed, which decomposes when the mixture is warmed, yielding the *anilide of monobromacetoacetic acid*, COMe·CHBr·CO·NHPh. This substance crystallises in plates, and melts at 138° with decomposition. *Isonitrosoacetoacetic anilide*, COMe·C(NOH)·CO·NHPh, crystallises in prisms, and is freely soluble in alcohol, ether, acetic acid, and light petroleum. It melts at 99—100°. On reduction with zinc and acetic acid, a crystalline compound, melting between 212° and 215°, is obtained.

The formation of *hydroxylepidine* (*γ-methylcarbostyril*),

$$C_9NH_5Me\cdot OH\ [Me : OH = 4' : 2'],$$

by the action of dehydrating agents on acetoacetic anhydride, has been already described (Abstr., 1884, 334 and 1198), and this substance has been described under the names of hydroxymethylquinoline and hydroxyquinaldine. On distillation with zinc-dust, it is converted into *γ-lepidine*, and it yields chlorolepidine when treated with phosphoric chloride (Abstr., 1885, 274). *Chlorolepidine*, C_9NH_5MeCl [Me : Cl = 2′ : 4′], melts at 59° and boils at 296° (corr.); it yields γ-methylquinoline when reduced with hydriodic acid, and also when decomposed by water at 200°.

Methoxylepidine, $C_9NH_5Me\cdot OMe$, formed by the action of potassium methoxide on chlorolepidine, is an oily liquid boiling at 275—276°. It forms a crystalline platinochloride. *Ethoxylepidine* melts at 51° and boils at 250° under 342 mm. pressure. Chlorolepidine reacts with aniline, forming *phenyllepidinamine*, a crystalline compound melting at 129—130°. The platinochloride melts at 235°.

Methyllepidone or *dimethylpseudocarbostyril*, $C_6H_4<\begin{matrix}CMe : CH\\NMe\cdot CO\end{matrix}>$, has already been described by the author as dimethylpseudoquinoxyl

(Abstr., 1885, 274). It can be prepared by the action of methyl iodide on hydroxylepidine, by the condensation of methylaniline and ethyl acetoacetate, and also by heating methoxylepidine at 280°. Methyllepidone melts at 130—132°, and sublimes without decomposition. It boils at 290° under 250 mm. pressure. It is a strong base, forming salts which are not decomposed by water. The platinochloride, $(C_{11}H_{11}NO)_2,H_2PtCl_6 + 3H_2O$, decomposes at 214—215°. Nascent hydrogen converts methyllepidone into a sparingly soluble crystalline compound, which melts at 258°. With bromine-water, methyllepidone forms *bromomethyllepidine*, $C_{11}H_{10}NOBr$. This compound crystallises in needles and melts at 172°. It is insoluble in water and alkalis, but dissolves in dilute acids and forms a crystalline platinochloride. On the addition of bromine to a solution of methyllepidone in chloroform, a dibromo-additive product appears to be formed. It is decomposed by warm water, forming monobromomethyllepidone.

The properties of methyllepidone, methoxylepidine, and lepidine are seen in the following table :—

	Methyllepidone.	Methoxylepidine.	Lepidine.
Boiling point	290° under 250 mm.	270°	253—255°
Melting point	130—132°	liquid	liquid
In steam	non-volatile	volatile	volatile
Odour	very faint	stupefying	penetrating,
Platinochloride	contains $3H_2O$, soluble in hot HCl	anhydrous, sparingly soluble	anhydrous, sparingly soluble
Bromine-water	monobromide	appears to form additive products	

W. C. W.

Metaquinolinecarboxylic Acid. By Z. H. Skraup and P. Brunner (*Monatsh. Chem.*, **7**, 519—520).—It is here shown that the seventh quinolinecarboxylic or the metaquinolinebenzocarboxylic acid, recently obtained by Tortelli from α-amidophthalic acid by means of the glycerol reaction, is also formed in small quantities, together with its isomeride, from meta-amidobenzoic acid, by means of the same reaction. In previous experiments, its formation was overlooked (Abstr., 1882, 71). V. H. V.

Synthesis of Active Conine. By A. Ladenburg (*Ber.*, **19**, 2578—2583).—Further experiments on a larger scale, and with pure materials, have confirmed the author's previous results (Abstr., 1886, 478). *α-Allylpyridine* boils at 187·5—192·5°, and is a strongly refracting liquid of sp. gr. 0·9595 at 0°, sparingly soluble in water, and having a distinct conyrine-like odour. The *platinochloride*, $(C_3H_5{\cdot}C_5H_4N)_2,H_2PtCl_6$, melts at 185—186°, and crystallises in needles sparingly soluble in water. The *aurochloride* melts at 135—136°; the mercuriochloride and cadmio-iodide are also described. By the action of sodium on an alcoholic solution at the boiling point, α-allyl-

pyridine is reduced almost quantitatively to *α-propylpiperidine*. This base has a sp. gr. 0·8626 at 0°, and boils at 166—167°; its hydrochloride crystallises in white, silky needles, melting at 203—205°. In smell, solubility, specific gravity, and physiological action, α-propylpiperidine resembles conine, and not only are the platinochlorides, aurochlorides, and cadmio-iodides similar, but when α-propylpiperidine is converted into conyrine by Hofmann's method, a blue fluorescence is obtained just as with conine. This fluorescence is due to an accompanying product, for if the fluorescent base after separation from unaltered conine be converted into the platinochloride, the conyrine regenerated from it is no longer fluorescent. Conyrine platinochloride from conine crystallises in monoclinic forms: $a : b : c = 1·0614 : 1 : 1·5374$; $\beta = 87° 8'$; and the crystals from the synthetical base give practically the same values on measurement.

α-Propylpiperidine, however, in addition to the lower melting point of its hydrochloride, is optically inactive, and must be regarded as a physical isomeride of conine. To effect a separation into two optically active bases, a sterilised nutritive solution containing 0·5 per cent. of the tartrate was seeded with *Penicillium glaucum*, but without result. The active base, however, was obtained by introducing a crystal of the salt into a very concentrated solution of α-propylpiperidine hydrogen tartrate; a slow separation of crystals took place, which yielded a dextrorotatory base, whose specific rotation was $[\alpha]_D = 13° 87'$, compared with $[\alpha]_D = 13° 79'$ for conine. The hydrochloride of the synthetical active base melts at 217·5°, that of conine at 217·5—218·5°.

From the mother-liquor, a lævorotatory base was obtained, but it contained a large proportion of the dextrorotatory modification, which could not be further separated by the crystallisation method. However, on converting this lævorotatory mixture into the cadmio-iodide, it was found that after crystallisation, the crystallised salt yielded a base which was less lævorotatory than before, whilst from the mother-liquor a base was obtained, which in a 50 per cent. alcoholic solution gave a rotation of $-3° 30'$ in a decimetre tube, compared with 3° 10′ for conine under the same conditions. W. P. W.

Reduction of Nicotine. By A. Liebrecht (*Ber.*, **19**, 2587—2598). —The author gives reasons for regarding nicotine as a *ββ*-hexahydrodipyridyl, in which one of the pyridine nuclei has taken up two, and the other four atoms of hydrogen. The author not having succeeded in obtaining dipyridyl by the oxidation of nicotine, has examined the complete reduction product obtained from its solution in absolute alcohol by the action of sodium (comp. Abstr., 1886, 161).

Dipiperidyl, $C_{10}H_{20}N_2$, is a colourless, oily liquid, solidifying at a low temperature, and having an odour like that of piperidine. It has a sp. gr. = 0·9561 at 4°, is lævorotatory, boils at 250—252° without decomposition, and is volatile to some extent with steam. In water, alcohol, and ether, it is readily soluble, and on exposure to light or the air it turns slowly yellow. Contrary to expectation, dipiperidyl acts only as a feeble poison. Dipiperidyl is a bi-acid base: its simple salts are very soluble and do not readily crystallise, although some

of the double salts crystallise well. The *hydrochloride* is very deliquescent; the *periodide*, $C_{10}H_{20}N_2,2HI,2I_2$, crystallises in brown needles, which lose iodine on drying in the air. The *platinochloride*, $C_{10}H_{20}N_2,H_2PtCl_6$, forms small, red prisms, which on rapid crystallisation, separate either singly or in staurolite-like groups: it melts at 202—203°. The *aurochloride*, $C_{10}H_{20}N_2,2HAuCl_4$, crystallises in yellow laminæ, melting at 131—132°, and is sparingly soluble in water. A mercuriochloride, $C_{10}H_{20}N_2,2HCl,5HgCl_2$, crystallises in small sparingly soluble tables. Carbon bisulphide combines with dipiperidyl, forming a yellow salt, easily soluble in water and alcohol, less soluble in benzene and insoluble in ether. It readily becomes resinified, and when its alcoholic solution is boiled with mercuric chloride, the odour of allylthiocarbimide is evolved.

Diacetodipiperidyl, $C_{10}N_2H_{18}Ac_2$, is prepared by heating the base with acetic anhydride at 170° for six hours. It is a yellow, oily liquid, boiling at 400—410° with slight decomposition, and does not solidify in a freezing mixture.

The action of methyl iodide results in the formation of the hydriodides of two bases, dimethyl- and trimethyl-dipiperidyl, of which the former is readily soluble, whilst the latter is insoluble in water.

Dimethyldipiperidyl, $C_{10}N_2H_{18}Me_2$, is an oil boiling at 230—332°, soluble in water in all proportions, and slightly volatile with steam. Its salts, with the exception of the *mercuriochloride*,

$$C_{10}H_{18}Me_2N_2,2HCl,2HgCl_2,$$

are readily soluble, and can scarcely be crystallised; the *platinichloride*, $C_{10}H_{18}Me_2N_2,H_2PtCl_6$, forms small dark red crystals.

Trimethyldipiperidyl, $C_{10}H_{17}Me_3N_2$, is obtained as a yellow oil of repulsive odour resembling that of methylamine, boiling at 205—212°; it is insoluble in water, and is not volatile with steam. The salts are very easily soluble and seem to be uncrystallisable, the *platinochloride*, $C_{10}H_{17}Me_3N_2,H_2PtCl_6$, is insoluble in alcohol and ether. The action of methyl iodide does not appear to yield a higher methylated base than trimethyldipiperidyl. W. P. W.

Sparteine. By E. Bamberger (*Annalen*, **235**, 368—376).—Sparteine was discovered by Stenhouse (this Journal, 1851, 213), and its compounds were afterwards investigated by Mills (this Journal, 1862, 1). The author has re-examined these bodies, and his results in many cases differ from the observations of Mills. Sparteine boils at 311—311·5°, under a pressure of 723 mm. The *sulphate*, $C_{15}H_{26}N_2,H_2SO_4$, forms large, transparent prisms, which are very soluble in water. The hydriodide, $C_{15}H_{26}N_2,HI$, forms glistening, four-sided plates, which probably belong to the rhombic system. It is freely soluble in alcohol and in hot water. When aqueous hydriodic acid acts on sparteine, a resinous mass is formed, from which the dihydriodide can be obtained in silky needles, by boiling the alcoholic solution with animal charcoal.

The compound $C_{15}H_{27}N_2EtI_2$, which Mills obtained by the action of ethyl iodide and alcohol on sparteine at 100°, is decomposed by

sodium hydroxide solution, forming an oily liquid, which can be separated into sparteine and sparteine ethiodide, by means of ether. *Sparteine ethiodide*, $C_{15}H_{26}N_2,EtI$, is formed by the action of ethyl iodide on sparteine. It crystallises in thick prisms, and dissolves freely in water and alcohol. Sparteine methiodide crystallises in rhombic plates; $a : b : c = 0{\cdot}8989 : 1 : 1{\cdot}6009$. The methyl hydroxide is a deliquescent substance, with a strongly alkaline reaction. The carbonate crystallises in needles. When sparteine is oxidised with potassium permanganate, the chief product is oxalic acid; acetamide is also formed, together with a small quantity of a pyridine-derivative.

W. C. W.

Pseudomorphine. By O. Hesse (*Annalen*, **235**, 229—232).—When potassium hydroxide (2 mols.) and potassium ferricyanide (1 mol.) are added to a solution of pure morphine hydrochloride dissolved in 40 parts of water, pseudomorphine is deposited; 100 parts by weight of morphine yield 88·4 parts of pseudomorphine. This result shows that the reaction takes place according to the equation $2C_{17}H_{19}NO_3 + 2KOH + 2K_3FeCy_6 = 2C_{17}H_{18}NO_3 + 2H_2O + 2K_4FeCy_6$ (the yield is theoretically 99·6 per cent.); not according to the following reaction: $2C_{17}H_{19}NO_3 + 2KOH + 2K_3FeCy_6 = C_{17}H_{17}NO_3 + C_{17}H_{19}NO_3 + 2H_2O + 2K_4FeCy_6$ (the yield is only 49·65 per cent. of the morphine employed). This shows that the formula for pseudomorphine is $C_{17}H_{18}NO_3{\cdot}C_{17}H_{18}NO_3$, as proposed by Polstorff (Abstr., 1889, 405), instead of $C_{17}H_{17}NO_3$, as formerly proposed by the author (Abstr., 1884, 616).

W. C. W.

Papaverine. By G. Goldschmiedt (*Monatsh. Chem.*, **7**, 485—505).—In this paper derivatives of papaveraldine, and the most convenient method for its preparation, are described.

The *nitrate*, $C_{20}H_{19}NO_5,HNO_3$, crystallises in citron-yellow needles; the *picrate*, in needles grouped together in voluminous aggregates; the *oxime*, $C_{20}H_{20}N_2O_5$, in flat, white needles melting at 245°; the *methiodide*, in golden prisms melting at 135° with decomposition; and the *ethobromide*, in large prisms melting at 270°.

Papaveraldine, if heated only for a short time with potash, yields veratric acid together with small quantities of a dimethoxyquinoline, the constitution of which is at present uncertain.

With tin and dilute hydrochloric acid, papaverine yields a tetrahydro-derivative, $C_{20}H_{25}NO_4$, which crystallises in small, white prisms melting at 200°, soluble in benzene and acetone, sparingly soluble in ether and petroleum. Its *hydrochloride* crystallises in transparent prisms of the monoclinic system, melting with violent decomposition at 290°; when injected internally, it causes albuminuria with inflammation of the kidneys. The *acid sulphate* forms acicular, and the *acid oxalate* prismatic crystals; the *dichromate*, glistening prisms; and the *picrate*, lemon-yellow needles. The *platinochloride* crystallises in minute yellow needles, and the *stannochloride* in concentrically grouped needles.

In an additional note, the author defends the formula $C_{20}H_{21}NO_4$ for papaverine, as against $C_{21}H_{21}NO_4$, that proposed by Hesse, Beckett,

and Wright, and others; exception is also taken to a statement of Hesse relative to the existence of an alkaloïd, pseudopapaverine.

V. H. V.

Papaverine Salts. By R. Jahoda (*Monatsh. Chem.*, **7**, 506—516).—As a further proof of the formula $C_{20}H_{21}NO_4$, proposed for papaverine, a number of its salts have been prepared and analysed; the results attained afford a strong confirmation of the above view.

The neutral *succinate* forms large tabular crystals melting at 171°, soluble in hot water; the *benzoate*, triclinic crystals ($a : b : c = 0{\cdot}459 : 1 : 0{\cdot}680$; $\eta = 95{\cdot}27°$), melting at 145°, soluble in alcohol, insoluble in water; the *salicylate*, monoclinic crystals ($a : b : c = 1{\cdot}161 : 1 : 1{\cdot}685$; $\eta = 102{\cdot}39$), melting at 130°; the *diodide* of the *hydroiodide*,

$$C_{20}H_{21}NO_4,HI,I_2,$$

purple crystals of the monoclinic system.

The hydrochloride gives with halogen salts of the metals double crystalline salts, of which the following are described:—The *cadmiochloride*, $(C_{20}H_{21}NO_4,HCl)_2CdCl_2$, small crystals, of the tetragonal system; $a : a : c = 1 : 1 : 0{\cdot}646$, melting at 176°; the *cadmio-bromide* and *-iodide*, white precipitates, melting at 150° and 180° respectively; and the *zincoiodide*, crystallising in small leaflets.

V. H. V.

Constitution of Cinchonine. By Z. H. Skraup (*Monatsh. Chem.*, **7**, 517—518).—The author criticises the view of Bischoff and Rach that cinchonic acid is β-γ-dicarboxyl-δ-valerolactone (Abstr., 1886, 1012); a study of the syrupy oxidation product of cinchonine and quinine has indicated the presence of an amorphous acid, $C_8H_{13}NO_4$, a base of the formula $C_9H_{17}NO_2$, difficult to obtain in the free state, although its salts form well-developed crystals, as also of a base of the formula C_9H_7NO, probably identical with kynurine, and an amorphous substance of the supposed composition $C_{13}H_{13}NO_2$, and of doubtful origin.

V. H. V.

Specific Rotatory Power of Piperidine Bases. By A. Ladenburg (*Ber.*, **19**, 2584).—The results obtained in a previous paper (this vol., p. 160) are in accordance with Le Bel-Van't Hoff's hypothesis, since α-propylpiperidine contains an asymmetric carbon-atom in its constitutional formula. As this is true of all α-alkyl-derivatives of piperidine, the author has examined α-pipecoline and α-ethylpiperidine, and by converting them into their dextrotartrates has succeeded in obtaining optically active modifications of each. Dextrorotatory α-pipecoline has a specific rotatory power of 21° 8′.

W. P. W.

Action of Bromine on Dimethylpiperidine; New Synthesis of Piperidine-derivatives. By G. Merling (*Ber.*, **19**, 2628—2632).—The author previously obtained (Abstr., 1884, 1385) by the action of bromine on dimethylpiperidine, two compounds—bromodimethylpiperidineammonium bromide and a hydrobromide. The latter is now shown to be dibromodimethylpiperidine hydrobromide. When the free base is warmed with alcohol, the alkaline solution becomes neutral, and characteristic crystals of monobromodimethylpiperidine-

ammonium bromide separate. These reactions can be explained by the constitutional formula assigned by Ladenburg to dimethylpiperidine: $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$. The constitution of dibromodimethylpiperidine and the ammonium bromide would then be

$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$ and $CH_2<\begin{matrix}CHBr{\cdot}CH_2\\ CH_2—CH_2\end{matrix}>NMe_2Br$.

The formation of the hydrobromide of dibromodimethylpiperidine is probably due to 2 mols. of the free base reacting with one another; this view was strengthened by the discovery of a base free from bromine in the last mother-liquor from dibromodimethylpiperidine hydrobromide.

N. H. M.

Hæmin Crystals. By K. Bikfalvi (*Chem. Centr.*, 1886, 499).—Blood free from chlorine yields no hæmin (chlorohæmatin) crystals when heated with glacial acetic acid. The author finds, however, that if NaCl, NaBr, KBr, NH_4Br, NaI, or KI be first added to the blood, crystals resembling chlorohæmatin are formed. L. T. T.

Diastase. By C. J. Lintner (*J. pr. Chem.* [2], **34**, 378—394).—The author has examined the different methods proposed for the preparation of pure diastase, and determined the diastatic activity of the substances obtained. He adopts Kjeldahl's law of proportionality (Abstr., 1880, 562), and uses the modification of Kjeldahl's method for determining diastatic activity, described in a former paper (Abstr., 1886, 386). In place of his former method for preparing soluble starch, he now recommends the following:—A quantity of pure potato-starch is mixed with a sufficient quantity of 7·5 per cent. hydrochloric acid to cover it; it is then allowed to remain for seven days at the ordinary temperature or for three days at 40°, when the starch has lost the power of gelatinising. The structure of the starch, however, remains unaltered. It is then well washed with cold water until every trace of acid is removed, and dried in the air. So obtained it is soluble in hot water to a bright and limpid solution. A 2 per cent. solution will remain clear for some days, but 10 per cent. solutions set to a jelly-like mass on cooling. The acid used must not exceed 7·5 per cent. as 10 per cent. acid causes the gelatinisation of the starch; with sulphuric acid, however, it requires at least 15 per cent. acid digested at 40° to effect the conversion into soluble starch. Lintner uses a 2 per cent. solution of this soluble starch instead of that prepared by the method previously given.

The diastatic activity of the precipitated diastases is expressed as 100, when 3 c.c. of a solution of 0·1 gram diastase in 250 c.c. water added to 10 c.c. of a 2 per cent. starch solution produces in one hour, at the ordinary temperature, sufficient sugar to reduce 5 c.c. of Fehling's solution. Diastase is best prepared from green malt or from air-dried malt. Lintner examined the preparation obtained from these malts by extraction with water and glycerol and subsequent precipitation with alcohol, both before and after heating at 70°, and obtained, in all cases, a substance with a comparatively slight diastatic activity. As the result of his experiments, he recommends the following method of preparation:—1 part of green malt or sifted air-dried malt is extracted with 2 to 4 parts of 20 per cent. alcohol for 24 hours. The filtered

extract is mixed with $2\frac{1}{2}$ volumes absolute alcohol; the precipitate quickly settles, and is washed on a filter with absolute alcohol; it is then transferred to a mortar, well mixed with absolute alcohol, thrown on a filter, and thoroughly washed with absolute alcohol and ether. Finally, it is dried in a vacuum over sulphuric acid. So obtained it is a light, yellowish-white powder with great diastatic activity. It is purified by repeated solution in water and precipitation with alcohol, and finally by dialysis. Loew's method of purification by means of precipitation with lead acetate is not to be recommended, since diastase loses three-fourths of its activity in the process. By purification, both the percentage of nitrogen and the diastatic activity are increased, whilst the amount of ash, which consists entirely of normal calcium phosphate, is diminished. A preparation obtained from green malt contained 8·3 per cent. nitrogen and diastatic activity = 96. After two precipitations the nitrogen = 9·06 per cent., and the activity = 100. This submitted to dialysis had the percentage of nitrogen raised to 9·9, and the percentage of ash diminished from 10·6 to 4·79. These and other analyses show that the diastatic activity increases with the amount of nitrogen. A purified diastase gave the following numbers on analysis, calculated on the ash-free substance. For the purpose of comparison the analyses of other soluble ferments are given:—

	C.	H.	N.	S.	
Diastase.....	46·66	7·35	10·42	1·12	(Lintner).
Pancreatic ferment	46·57	7·17	14·95	0·95	(Hüfner).
Invertase	43·9	8·4	9·5	0·6	(Barth, Donath).
Emulsin	43·5	7·0	11·6	1·3	(Bull).

Diastase gives all the reactions for the albuminoïds, but not the characteristic biuret reaction for peptones; it gives, however, a characteristic blue coloration with tincture of guaiacum and hydrogen peroxide, which is soluble in ether, benzene, chloroform, and carbon bisulphide, but not in alcohol. This reaction is given by no other soluble ferment or proteïn substance. G. H. M.

Note.—Lintner appears to have overlooked the fact that O'Sullivan (this Journal, Trans., 1884, 2) described an almost identical method of preparing pure diastase. G. H. M.

Action of Diastase and Invertin. By H. Muller (*Ann. Agronom.*, **12**, 481—482).—The author has studied the action of these ferments under conditions such as prevail in the plant-cell, with a view to elucidate their physiological importance. Both ferments are active at 0°, but the activity increases until the neighbourhood of 50° is reached: the temperatures being 0°, 10°, 20°, 30°, 40°; the energy of diastase is expressed by the numbers 7, 20, 38, 60, 98, and that of invertin by the numbers 9, 19, 36, 63, 93.

Under ordinary conditions, cell-sap contains much carbonic anhydride, and is exposed to a pressure of several atmospheres. Both of these circumstances accelerate the activity of the ferments. Even at the ordinary pressure, saturation of the liquid with carbonic anhydride may have the effect of tripling the energy of diastase, and in presence

of carbonic anhydride diastase has the power of acting on starch which has not been boiled to a paste. Between the limits of 2 and 20 per cent., concentration of a sugar solution has little effect on the action of invertin, which is a little more feeble in strong solutions than in weak ones, but the accumulation of invert sugar is strongly opposed to the continuance of the reaction. J. M. H. M.

Physiological Chemistry.

Natural and Artificial Digestion. By T. Pfeiffer (*Zeit. physiol. Chem.*, **11**, 1—24).—The author has previously criticised the work of Stutzer on this subject (see Abstr., 1886, 1053). Additional experiments on pigs are now brought forward, and from them the following results are drawn:—

1. A comparison of the method of natural digestion of the nitrogenous constituents of the food combined with the investigation of the products of metabolism, with the method of artificial digestion of the food-stuff by pepsin and trypsin as devised by Stutzer, shows that there is an almost absolute agreement between the two.

2. By the help of Stutzer's method, the digestibility of the nitrogenous constituents of the food can be estimated with sufficient accuracy. This always gives results which agree more closely than those obtained with the method hitherto used, in which the products of nitrogenous metabolism in the fæces are not investigated.

W. D. H.

Glycogen in the Liver of New-born Dogs. By B. Demant (*Zeit. physiol. Chem.*, **11**, 142—144).—In the intra-uterine condition, the liver is stated to be very poor in glycogen. Hoppe-Seyler states the opposite to be the case. The present research investigates the matter in the case of the dog; the glycogen was estimated by Brücke's method, and the result found was that in the days following birth glycogen was present in exceedingly large quantities; this is illustrated by the following table:—

Age of animal.	Percentage quantity of glycogen in the liver.
1 hour	11·389
3½ hours	9·527
3 hours	5·443
4 days	2·627
11 „	2 792
12 „	3·664
Fully grown	1·661

W. D. H.

Lactic Acid in Animals. By A. Hirschler (*Zeit. physiol. Chem.*, **11**, 41—42).—Lactic acid has been described as occurring in the grey matter of the brain, and in the parenchymatous juices of the spleen, thymus, lymphatic glands, &c. Which variety of lactic acid this is,

has not yet been investigated. The present research is concerned with this question in relation to the spleen and lymphatic glands of the ox. Lactate of zinc was obtained by Hoppe-Seyler's method, with the modification that the finely chopped organ was extracted by 0·5 per cent. sulphuric acid instead of by cold water; in this way, more lactic acid is obtained. By estimation of the water of crystallisation of the zinc salt, and of the hydrogen and carbon, the conclusion is drawn that both in the spleen and lymphatic glands it is sarcolactic acid which is present. W. D. H.

Pigments of Melanotic Sarcomata. By K. A. H. Mörner (*Zeit. physiol. Chem.*, **11**, 66—140).—The name *melanin* has been hitherto used for the pigments occurring in the eye, hair, and skin, in pathological new growths, and also for the decomposition products of chromogens in urine. The black pigment of the retina has been investigated by Berzelius, who found it contained a small quantity of iron, by Scherer who found no iron, and also by Rosow and Sieber. The percentage composition obtained by the various observers shows great discrepancies, and this, with their methods of preparing the pigment, renders it probable that they were not dealing with a pure substance. Concerning the black pigment of the skin of negroes and of the hair, still less is known, and although some few percentage estimations have been made by Sieber, the result cannot be described as a convincing one.

The pigment of melanotic tumours was first investigated by Heintz, who found that it was soluble in alkalis with difficulty, and that it contained no iron. An elementary analysis gave the following figures: C = 53·40, H = 4·02, and N = 7·10 per cent. Dressler made a similar investigation, and found in the pigment a small quantity of iron. Berdez and Nencki named the pigment *Phymatorusin;* they found it to be insoluble in water, alcohol, and ether, easily soluble in solutions of fixed alkalis or their carbonates, and in ammonia; from such solutions it was precipitable by acids, but was somewhat soluble in excess. The preparation contained carbon, hydrogen, oxygen, and nitrogen, sulphur in large amount (10·67 per cent.), but no iron, phosphorus, or chlorine. In horses, they found in melanotic tumours a pigment with somewhat different properties, which they called *hippomelanin.*

In the urine of some of these patients, a pigment has been found which according to some is an excess of the ordinary urine pigments, and according to others is the same pigment that occurs in the tumour. It is turned a dark-brown colour by the action of nitric acid; and in some cases a similar change occurs after mere exposure. The uncertain and contradictory statements of previous observers cannot but render uncertain which of the above statements is correct. Again, in other cases of these tumours, particles of a brown pigment are found in the blood, the corpuscles having the normal shape and colour; similar granules have been occasionally described in the urine and urinary passages.

The present research was undertaken with the material supplied by a patient, the full particulars of whose case are given. During life, the urine showed the peculiar coloration above-mentioned; after

death, the tumour itself was investigated. Its situation was the shoulder; secondary growths were present in the liver, but none in the kidney substance. The blood, except for a low percentage of hæmoglobin, was normal. The colouring matter did not give any absorption-bands, but produced a general dimming of the spectrum, especially towards the violet end. The methods by which the pigment was investigated were: first, by the spectrophotometer to determine the extinction coefficients in different parts of the spectrum; and, secondly, by elementary analysis. Although the quantity of material at hand was small, and therefore some results are incomplete, and others put forward with reserve, yet certain definite conclusions were arrived at. The pigment was found to contain iron, which also was estimated spectrophotometrically, as well as by the usual methods; the spectrophotometric method consisted in converting the iron of the ash into ferric thiocyanate, and comparing its extinction coefficients with those obtained from a solution of ferric chloride of known strength similarly treated. Iron was present in small quantities; the failure of some previous observers to obtain the proof of its presence is accounted for by their having used hydrochloric acid in the preparation of the pigment. It is found that this acid dissolves out nine-tenths of the iron from the pigment.

Baryta-water causes a precipitate in the urine, and this carries down with it a good deal of the pigment; this is filtered off. In the filtrate, the remaining portions of the pigment are carried down with the precipitate caused by lead acetate. For the method adopted for separating the pigment from the tissues of the tumour, the original paper must be consulted. The pigment obtained from these three sources is a brownish, amorphous powder when dry. It is partly soluble in acetic acid, and partly insoluble.

The following table represents the percentage composition, and the relative absorption for the region wave-length = 562, for these different preparations:—

	C.	H.	N.	S.	Fe.	Absorption.
	Percentages.					
A. *Pigment insoluble in acetic acid*—						
1. From the tumour.....	55·72	6·00	12·30	7·97	0·072	0·00038
2. From the baryta precipitate.	55·76	5·95	12·27	9·01	0·20	0·00039
3. From the lead precipitate ..	—	—	—	8·30	0·25	0·00029
B. *Pigment soluble in acetic acid*—						
3. From the tumour.....	—	—	—	5·90	0·21	0·00094
4. From the baryta precipitate.	—	—	—	—	0·19	0·00114
5. From the lead precipitate ..	58·07	8·03	11·08	4·75	0·20	0·00056

There are thus two pigments, although perhaps it may be that the

two are produced from a mother-substance by the action of the acid. They differ from one another in percentage composition, and in absorptive power. They resemble one another in solubilities, except with regard to acetic acid, and in colour to the naked eye. The high percentage of sulphur in the pigment insoluble in acetic acid agrees with the similar condition in phymatorusin. An important point brought out is the identity of the tumour pigment with that in the urine; it is probably brought to the urine by the blood, in which feebly alkaline liquid it is slightly soluble. It is not the same pigment as occurs in normal urine; that gives quite a different spectrophotometric chart. W. D. H.

Cobra Poison. By C. J. H. Warden (*Chem. News*, **54**, 197—199; 209—211).—Two samples of air-dried snake-venom contained respectively 16·26 and 15·43 per cent. of water. Fresh venom yields 25—50 per cent. of solid residue. For the author's experiments, the solution of the dried venom in distilled water was injected under the skin of the back of white or piebald China mice. A dose of 0·012 gram of anhydrous venom was fatal in four minutes, and the rapidity of action decreases as the quantity of poison administered is diminished; with 0·000016 gram, the animal may live three hours, whilst 0·000008 gram is not fatal. Very large and very small doses cause convulsions, intermediate doses do not. In the case of white mice, the fatal ratio of poison to body weight appears to be about 1 : 10,000,000. Heating the solution of the venom soon produces marked coagulation, but it is only after heating for some time that the toxic activity is reduced, hence prolonged heating at a moderate temperature is more effective for such a purpose than short periods at higher temperatures. Similar remarks apply to the action of picric acid, which causes an abundant precipitate in solutions of the poison, and in some experiments a marked reduction in the toxic action when the filtered solution was employed. D. A. L.

Urine of the Tortoise. By T. W. Mills (*J. Physiol.*, **7**, 453—457).—The urine of the tortoise is liquid, ranging in colour from colourless to light amber, and is of an acid reaction. In some cases, it is green from admixture with bile in the cloaca. Albumin is invariably present; although probably this is derived from the intestine, *viâ* the cloaca. On allowing the urine to stand, the albumin having been removed, a deposit of uric acid crystals, of an orange colour occurs. On many occasions uric acid crystals were found in the urine without any treatment; these were always colourless. By Heintz's hydrochloric acid method, the amount of uric acid in the urine was estimated, and found to be several times greater than in human urine. Urea is altogether absent. The inorganic constituents do not differ in kind from those found in the urine of man.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Reduction of Copper Sulphate during Alcoholic Fermentation. By H. Quantin (*Compt. rend.*, **103**, 888—889).—In experiments on a small scale, it is found that copper existing in the form of copper sulphate to the extent of 0·05 gram per litre, is completely precipitated in the form of copper sulphide during alcoholic fermentation. On a large scale, doubtless a still larger quantity would be removed, but the quantity given is greater than would ever be introduced into the wort as a result of the use of copper sulphate as a remedy for mildew. Since moist copper sulphide is readily oxidised, it is important to avoid any aëration of the lees containing it. The sulphide is the only salt of copper which is insoluble in the must of grapes. C. H. B.

Alcoholic Fermentation of Dextrin and Starch. By U. Gayon and E. Dubourg (*Compt. rend.*, **103**, 885—887).—The authors have met with a species of *Mucor* which has the power of converting dextrin and starch into sugar, and then fermenting the sugar but, like *Mucor circinelloides*, it has not the power of inverting cane-sugar, and transforming it into alcohol. Other non-inversive ferments, on the other hand, have not the power of fermenting dextrin and starch. In beer wort or solutions of glucose, this mucor develops rapidly in large, spherical, ferment cellules. In dextrin or starch, it at first forms mycelial tubes, which soon swell up, divide, and form themselves into globular masses. In yeast-water containing sugar, the mucor forms only a bulky, unicellular mycelium.

The fermentation of dextrin takes place somewhat slowly, and that of starch requires still longer. The dextrin existing in beer is readily saccharified by this mucor and converted into alcohol, if the alcohol already in the beer is expelled before adding the ferment.

Eurotium oryzæ, used in the manufacture of "koji," secretes a diastase which converts rice into a true malt, and this plant also inverts cane-sugar, but it cannot carry fermentation any further.

C. H. B.

Method of Preventing Secondary Fermentations. By U. Gayon and G. Dupetit (*Compt. rend.*, **103**, 883—885).—The addition of tannin in quantities of 0·5—1·0 gram per litre gives good results, but does not prevent the development of *Mycoderma aceti*.

Salts of bismuth, even in small quantities, completely prevent secondary fermentations. The addition of 0·1 gram of basic bismuth nitrate per litre almost entirely prevents any increase in the acidity of the wort, and by keeping the yeast pure produces a distinct increase in the proportion of alcohol. The character of the results is seen from the following table. The first column in each set of experiments shows the behaviour of the wort containing the bismuth salt, and the second column shows the behaviour of the ordinary wort:—

	A.		B.		C.	
Capacity of vat in hectolitres	600	600	200	200	200	200
Source of molasses.....	beetroot	beetroot	cane	cane	cane	cane
Density of molasses wort.....	1075	1075	1060	1060	1060	1060
Proportion of maize wort.....	0·1	0·1	0·25	0·25	0·25	0·25
Density of maize wort	1031	1031	1029	1030	1035	1034
Maximum temperature.....	35°	35°	32°	33°	33°	32·5
Increase of acidity.....	2·5	13·0	6·7	26·5	4·5	36·0
Percentage of alcohol in product .	5·87	5·74	4·94	4·71	4·96	4·37
Difference in amount of alcohol ..	−0·13		−0·23		−0·59	

C. H. B.

Is Free Nitrogen formed during Putrefaction? By A. Ehrenberg (*Zeit. physiol. Chem.*, **11**, 145—179).—Considering the important part that nitrogen plays in the organisms of plants and animals, many researches have been undertaken to determine, first, whether the atmospheric nitrogen takes any part in the nutrition of organisms, especially low organisms like bacteria, or whether as a result of decomposition, nitrogen in the free state is formed; the conclusions drawn by various workers are most contradictory. The present research is devoted only to the investigation of the question as to whether nitrogen is formed in putrefactive processes. The author intends to pursue the subject further in relation to nitrification. By means of an apparatus, which is described and figured, the use of caoutchouc stoppers is dispensed with, as diffusion takes place through these; wherever a stopcock is necessary, it is immersed in a trough of mercury. The gases formed by various putrefying mixtures were analysed. The method of gas analysis is preferable to that of nitrogen estimations, since certain nitrogenous compounds, formed by putrefaction (*e.g.*, of the quinoline and pyridine groups), undergo dissociation at a high temperature. The substances investigated were dried blood moistened with cow's urine, cow's urine alone or mixed with calcium carbonate, and the dung of horses and cows. These substances were mixed with some liquid in which putrefaction was taking place, and the investigation carried out in the presence of pure oxygen, so that only the aërobic organisms could act; carbonic anhydride was formed, but no nitrogen. In other experiments carried out in the absence of oxygen on a mixture of broth, sugar, peptone, sodium phosphate, sodium chloride, and sodium nitrate, it was also found that no nitrogen was formed. These experiments were carried out in an atmosphere of carbonic anhydride, in which only the anaërobic bacteria would be able to act. It was also found that during the slow combustion of organic materials no nitrogen was formed. W. D. H.

Absorption of Carbonic Anhydride by Leaves. By P. P. Dehérain and Maquenne (*Ann. Agronom.*, **12**, 526—534).—The authors cite determinations which confirm the conclusions already arrived at by them, namely, that the absorption of carbonic anhydride

by vegetable tissues is a true phenomenon of solution, varying with the temperature, as in all cases of absorption of gas by an inert solvent, and which, consequently, when the leaf respires in an atmosphere kept at constant pressure, gives rise to a supersaturation comparable with that of a mass of water into which calcium carbonate and hydrochloric acid have been introduced simultaneously.

This absorption of carbonic anhydride by leaves is extremely rapid, at any rate when the leaves are in a vacuum, in consequence of the large surface exposed. J. M. H. M.

Ripening of Seeds. By A. Muntz (*Ann. Agronom.*, **12**, 399—400).—Unripe rye grain contains a notable proportion of synanthrose, a sugar analogous to cane-sugar, and only found up to the present in the roots or tubercles of certain Synantheraceæ. The synanthrose in the dry grain was on May 25th 45 per cent. to 21·55 per cent. starch, and on July 12th 6·85 per cent. to 68·78 per cent. starch. There is still some synanthrose in the ripe grain after being kept for months. The unripe grain of wheat also contains synanthrose, which, however, does not persist, but is gradually replaced by cane-sugar; wheat also contains an inverting ferment capable of transforming synanthrose into reducing sugars. 200 grains of wheat weighed after desiccation at 9 A.M. 10·042 grams; after exposure to the sun for 12 hours they weighed 8·648 grams, the loss being due to slow combustion. The young colza seed contains cane-sugar and a reducing sugar having the rotatory power of invert sugar; at maturity, cane-sugar alone remains. By determining from time to time the sugar, starch, fat, and nitrogenous matter in a constant number of colza seeds during an increase in weight from 121 mgrms. to 498 mgrms., the author finds that the glucose diminishes gradually and disappears, the cane-sugar increases, the starch, always present in small quantity, gradually diminishes, the nitrogenous and fatty matters constantly increase. It, therefore, appears that the seed itself does not contain the carbohydrates which undergo transformation into oil; but analyses of the pod or siliqua at various dates show that sugar and starch constantly flow there, and disappear after a short sojourn, thus probably furnishing the material out of which the oil of the seed is elaborated.
J. M. H. M.

So-called Soluble Starch. By J. Kraus (*Ann. Agronom.*, **12**, 540—541).—Janis and Schenk have found in the epidermis of *Ornithogalum* and of *Gagea* a substance dissolved in the cell sap which strikes a blue colour with iodine. Nägeli has shown that it is not starch, and believes it to be an albuminoïd. The author, having met with this same substance in the epidermis of some *Arums*, has come to the conclusion that it is allied to the tannins. Chloriodide of zinc colours it rose, ferric chloride and ferrous sulphate strike a brownish-green; on the other hand, potassium dichromate and Gardiner's reagent give no reactions. The substance behaves like a tannin in being developed under the influence of light, and in persisting without alteration in dead or dying leaves. That iodine should strike a blue colour with a tannin is not surprising, since Giessmayer has shown that a solution of tannin gives with a weak solution of iodine, in feebly

alkaline water, a bright red colour, and Nasser has recognised that tannic and gallic acids and pyrogallol, in the presence of neutral salts or acids, are coloured red-purple by iodine. J. M. H. M.

Substances contained in the Roots of Hydrastis Canadensis. By M. Freund and W. Will (*Ber.*, **19**, 2797—2803).—Perrins (*Pharm. J. Trans.* [2], **3**, 546) obtained from the root of *Hydrastis*, berberine and another alkaloïd to which he ascribed the name hydrastine. The authors found that the latter is best obtained by extracting the finely powdered roots with ether. It melts at 132° and crystallises in the rhombic system; $a : b : c = 0{\cdot}8461 : 1 : 0{\cdot}3761$. The solution in chloroform (1·2759 gram to 50 c.c.) has a rotatory power $[\alpha]_D = -67{\cdot}8°$; in aqueous hydrochloric acid, $[\alpha]_D = +127{\cdot}3°$. Analyses of the compound confirm the formula $C_{22}H_{23}NO_6$, ascribed to it by Mahla (*Amer. J. Sci.* [2], **36**, 57). It reacts with methyl iodide, yielding the compound $C_{22}H_{23}NO_6,MeI$. This crystallises from alcohol or water in needles melting at 208°. When hydrastine is dissolved in hydrochloric acid and treated with potassium permanganate, it is converted into opianic acid. Nitric acid acts on hydrastine, yielding a *base* melting at 115°, very readily soluble in chloroform, alcohol, and ether. Hydrastine is not changed when fused with potash. These experiments show that great analogy exists between hydrastine and narcotine.

Another compound was isolated from the roots of the *Hydrastis;* it crystallises well and melts at 100°. It does not contain nitrogen. It dissolves unchanged in hot strong hydrochloric acid and in warm aqueous potash, and appears therefore to be a lactone.

N. H. M.

Valuation of Manures. By P. P. Dehérain (*Ann. Agronom.*, **12**, 436—444).—The author expresses the value of a manure or manurial constituent for a particular soil or crop in the following manner. If R is the yield per hectare on the manured plot, and R′ that on the unmanured plot, V the price of the produce, and P the weight of manure used, then the value of the unit of weight of the manure for that soil and crop is $\frac{(R-R')V}{P}$. In the case of nitrogenous manures, if N, the weight of nitrogen in the manure, be substituted for P in the above expression we get as quotient the value of the unit of nitrogen in that particular form and case. Applying this method to the results of field experiments at Grignon, the author shows the different values that the unit of nitrogen may have in different forms and under different circumstances. Thus with green maize in 1879—

	fr.	c.
The kilo. of nitrogen in farmyard manure was worth....	6	60
„ „ nitrate of soda „	2	34
„ „ flesh manure (large dressing) ..	0	88
„ „ „ „ (small „) ..	1	43

The experiments with oats from 1875—1879 yield the following values:—

	fr.	c.	
Nitrogen in farmyard manure.....	3	26	per kilo.
„ nitrate of soda.....	3	68	„
„ mixture of the two.....	4	17	„

J. M. H. M.

Production of Farmyard Manure. By A. Muntz and C. Girard (*Ann. Agronom.*, **12**, 429—436).—By exact experiments, the authors have sought to establish the proportions of the total manurial elements in the food consumed which become stored up in the increase of live-weight, recovered in the manure, and lost. The food given was weighed and analysed, the increase of live-weight or the quantity of milk yielded during the duration of the experiments noted, and the manure carefully collected and analysed. The following results were obtained: 32 sheep kept in a fold with asphalt floor so as to prevent loss of manure, gave the following results:—

Nitrogen consumed.....	21·817 kilos.		
„ converted into flesh..	4·300	„	= 21·7 per cent.
„ recovered in manure.	5·588	„	= 19·72 „
„ lost.....	12·129	„	= 55·58 „

Some of this great loss of nitrogen is due to escape into the air of ammonium carbonate; the air of the fold was found to contain about 0·008 gram ammonia per cubic metre, or 400 times as much as normal air.

Two Normandy cows were each fed daily with 53½ kilos. of lucerne and 49 kilos. of water, and each furnished 33 kilos. of solid excreta and 18 kilos. of urine. The weight of the animals increased by 15 kilos. during the experiment, and they furnished 361 litres of milk.

	kilos.		
Nitrogen consumed.....	14·146		
„ assimilated as flesh..	0·544	3·104	= 21·95 per cent.
„ „ in milk..	2·560		
„ in manure.....	7·461		= 52·75 „
„ lost	3·581		= 25·30 „

The loss is much less than in the case of the sheep, probably because the fermentation being less active, less ammonium carbonate is formed.

Quantity of Fertilising Matter supplied to the Soil by Grazing Sheep.—With a ration of green lucerne and straw litter, 2·230 kilos. of manure were produced for 4·085 kilos. of lucerne consumed and 0·9 kilo. of water drunk. The sheep increased in weight 30 kilos.

The phosphoric acid in the forage was 2·952 kilos., and in the manure 2·955 kilos.; the potash in the forage 13·002 kilos., and in the manure 15·280 kilos., there was therefore no loss of these fertilising constituents; the distribution of the nitrogen was as under:—

	kilos.		
Nitrogen consumed.....	14·548		
„ assimilated as flesh....	1·089	= 7·50	per cent.
„ in manure	6·349	= 43·64	„
„ lost	7·110	= 48·87	„

With an earth litter the loss of nitrogen was much less, as the following figures show :—

	kilos.	
Nitrogen consumed.....	13·707	
„ fixed by animal	1·379	= 10·06 per cent.
„ in manure	9·042	= 65·96 „
„ lost	2·376	= 23·98 „
Phosphoric acid in fodder	2 820	
„ „ manure.....	3·260	
Potash in fodder	13·235	
„ manure.....	12·017	

The advantage of earth litter over straw litter, and of the custom of folding on the soil instead of stabling, is demonstrated by these experiments.

With lucerne hay and straw litter, the following results were obtained.

	kilos.	
Nitrogen consumed.....	23·011	
„ fixed by animal	1·670	= 7·25 per cent.
„ in manure	8·899	= 38·67 „
„ lost	12·442	= 51·08 „

J. M. H. M.

Manurial Value of Basic Steel Slag. By J. Wrightson and J. M. H. Munro (*Ann. Agronom.*, **12**, 488—495).*—The basic steel cinder or Thomas slag employed in these experiments had the following composition :—CaO, 41·54; MgO, 6·13; Al_2O_3, 2·60; FeO, 14·66; F_2O_3, 8·64; MnO, 3·81; V_2O_3, 0·29; SiO_2, 7·40; P_2O_5, 14·32; SO_3, 0·31; S, 0·23; total 99·93. Side by side with this were tried ground Cambridge coprolites containing 25·1 per cent. P_2O_5; mineral superphosphate of ordinary quality containing 12·0 per cent. soluble P_2O_5; rich (Curaçoa) superphosphate containing 20·1 per cent. soluble P_2O_5; and also precipitated phosphate of lime prepared from basic cinder by Scheibler's process. This precipitated phosphate contained 30·89 per cent. P_2O_5, with CaO, 29·91; Fe_2O_3, 3·62; SiO_2, 7·53; water, 18·72; the P_2O_5 in this product is practically all soluble in ammonium citrate. The experiments were made in duplicate on a thin, light, chalky soil at Downton (Wilts), and on a stiff clay nearly destitute of lime at Ferryhill (Durham), with plots $\frac{1}{10}$ acre in area. Duplicate plots of each dressing were employed at both stations; there were 35 plots in each series, and they were so arranged as to permit a comparison of every manured plot with one or more *adjacent* unmanured plots; the special comparisons between the different manures were also obtained from *adjacent* plots. Swedes were grown at Downton, and yellow Aberdeen turnips at Ferryhill; the mean yield of the six *unmanured* Downton plots was 2360 roots, weighing 6 cwts. 0 qr. 14 lbs., and that of the six *unmanured* Ferryhill plots was 362 roots, weighing 2 cwts. 2 qrs. 7 lbs. On the unmanured plots at Ferryhill, most of the young

* "Report of Experiments made to ascertain the manurial value of Basic Cinder produced at the works of the North Eastern Steel Co., Limited," Middlesborough, 1886.

plants were unable to withstand the attack of the fly, on the manured plots, failure from this cause did not take place. The following table shows the *mean* increases over the unmanured plots obtained both at Downton and Ferryhill with the different manures :—

	lbs. P_2O_5.	Increase per plot $\frac{1}{10}$ acre.					
		Downton.			Ferryhill.		
		cwts.	qrs.	lbs.	cwts.	qrs.	lbs.
2 cwts. basic cinder.....	32·0	9	2	20	12	1	14
54 lbs. superphosphate.....	6·5	8	3	15	14	0	21
35 lbs. precipitated phosphate..	10·9	7	0	20	10	3	7
45 lbs. superphosphate.....	5·4	5	3	25	9	1	7
45 lbs. basic cinder	6·5	5	0	3	11	0	21
28 lbs. rich superphosphate....	5·6	4	2	15	10	1	7
17 lbs. precipitated phosphate..	5·3	3	3	13	9	0	21
78½ lbs. basic cinder.....	11·2	2	3	5	10	1	15
45 lbs. ground coprolites	11·2	0	1	2	8	2	0

At Downton, on a thin, chalky soil, it will be seen that 4 cwts. per acre of basic cinder was a little inferior to an equal weight of superphosphate, but vastly superior to the same quantity of ground coprolites. If dressings of these manures containing equal weights of phosphoric acid are compared, it is found that the unit of P_2O_5 in basic cinder is a little inferior in efficiency to that in superphosphate, inferior also to that in precipitated phosphate, but decidedly superior to the unit of phosphoric acid in ground coprolites. Making the same comparisons at Ferryhill on this clay soil, deficient in lime, it is found that *soluble* phosphoric acid loses a great deal of its superiority over the insoluble forms. 4 cwts. per acre of basic cinder is actually a better manure than an equal weight of superphosphate, and but very little inferior to a dressing of superphosphate containing an equal weight of phosphoric acid; in fact, on this soil, soluble phosphate, cinder phosphate, and precipitated phosphate are very near each other in efficiency, with coprolite phosphate a little way behind. At Downton, a heavy dressing of basic cinder gave the best result, at Ferryhill, a dressing of 4 cwts. per acre was almost as efficacious as one of 20 cwts. per acre. The general conclusion deducible from these experiments is that phosphoric acid exists in basic cinder in a condition to be easily assimilated by plants, and that in this respect it resembles soluble phosphoric acid and precipitated phosphoric acid much more than the insoluble phosphoric acid of ground mineral phosphates, hence Thomas-slag is likely to occupy an important position as a phosphatic manure. In the two years 1884 and 1885 there were no signs of injury to the crop even from the heaviest dressings of basic cinder, namely, 1 and 2 tons per acre. Besides the precipitated phosphate prepared from basic cinder, two other patented preparations were included in the series of experiments, but in view of the very striking results obtained with

the raw ground cinder, these proposals lose much of their interest. According to one of these patents (Munro and Wrightson, No. 250, A.D. 1885), ground basic cinder is used as a precipitating agent for the soluble phosphoric acid of rich superphosphate, and by mixing the two substances in suitable proportions, a manure of moderate richness is obtained, free from any excessive proportion of oxides of iron, and containing phosphoric acid in three highly assimilable forms,—soluble, "precipitated," and cinder phosphoric acid. The plots on which this manure was tried show that the efficacy of the soluble phosphoric acid was not weakened by partial precipitation, and that the cinder phosphoric acid in the compound manure exercised a manurial effect over and above that due to the phosphoric acid of the superphosphate. The manufacture of a superphosphate from basic cinder itself has also been tried and patented (Munro, No. 7740, A.D. 1885). When treated with the proper quantity of sulphuric acid, basic cinder is converted into a light green, dry, friable, and very open substance containing a large proportion of calcium sulphate, soluble phosphate of lime, and about 12 per cent. of crystallised ferrous sulphate. (A portion of the phosphoric acid exists as soluble ferrous phosphate.) In view of the recent experiments of Griffiths, it was thought that the ferrous sulphate contained in this manure might exert a beneficial effect on vegetation, instead of being, according to the common belief, an absolute poison. The effect of ferrous sulphate on vegetation seems to depend on the dose, a small quantity being sometimes beneficial, and a large one invariably noxious. On the experimental plots to which the "dissolved cinder" was applied, the effect of the ferrous sulphate appeared to be uniformly disadvantageous. The dissolved cinder in all cases had *some* manurial value, giving increases over the unmanured plots, but these increases were less than were obtained with the same quantity of cinder not dissolved by acid, so that the sulphate of iron appears to have neutralised a part of the benefit derived from the phosphoric acid. J. M. H. M.

Influence of the Ferrous Oxide in Basic Cinder on the Growth of Plants. By J. M. H. Munro (Middlesborough, 1886).—This report contains experiments supplementary to those which formed the subject of the preceding Abstract. Seeds of various sorts—barley, white turnips, clover, white mustard, garden cress—were sown in mixtures of garden soil with basic cinder, in order to ascertain whether the large proportion of ferrous oxide in the basic cinder exercises any unfavourable influence on germination or growth. In order to put this question to the severest test, enormously exaggerated doses of basic cinder were employed, namely, 10 per cent. of the mixed soil, 25 per cent., 50 per cent., and pure basic cinder without any soil. Most of the seeds tried germinated even in the pure basic cinder, and some of the plants lived until starved for want of nitrogenous food. All the other mixtures produced plants which flowered and seeded in due course—the barley plants in the mixture of equal parts of basic cinder and garden soil were actually better than those grown in garden soil alone, and produced full ears of grain of unimpaired germinating power. Since basic cinder is an alkaline substance containing free

lime, it is only natural that in the three strongest mixtures fewer seeds germinated than in the three weaker mixtures or in garden soil alone. The conclusion arrived at is that the ferrous oxide contained in basic cinder is without injurious influence on germination or growth. J. M. H. M.

Analytical Chemistry.

Apparatus for Gas Analysis. By O. Pettersson (*Zeit. anal. Chem.*, **25**, 479—484).—The principle on which the measurements are made is similar to that employed for air analysis (this vol., p. 180). The standard volume of air is, however, contained in a special bulb connected with the eudiometer through the differential manometer. The gas is introduced by a side tube from a bell-glass inverted in a mercury trough. The absorptions take place in Orsat tubes connected with the eudiometer by stopcocks. There are also wires for explosions. M. J. S.

Universal Spectroscope for Qualitative and Quantitative Chemical Analysis. By G. Krüss (*Ber.*, **19**, 2739—2746).—A modified form of Bunsen and Kirchhoff's spectroscope is described with sketches.

New Volumetric Method for Determining Fluorine. By F. Oettel (*Zeit. anal. Chem.*, **25**, 505—511).—The fluorine is measured as silicon fluoride in a special form of eudiometer. The decomposition vessel is a stoppered flask with the neck above the stopper enlarged into a cup for holding mercury. A tube branching from the neck is ground into the top of the eudiometer, the joint being also covered with mercury. The eudiometer is connected at its lower end with a mercury tube like that of the nitrometer. The graduation begins 10 c.c. below the top of the eudiometer, and 10 c.c. of sulphuric acid are introduced above the mercury. To obtain sulphuric acid suitable for the decomposition, ordinary acid is heated with sublimed sulphur until it begins to fume, then poured off from the fused sulphur and evaporated to two-thirds of its volume. The fluoride (which if decomposable by cold acid may be enclosed in a tube sealed by a drop of fused acid potassium sulphate) is placed in the flask with ignited quartz-powder. After reading the mercury level and temperature, 50 c.c. of acid is added and the stopper inserted. The acid is slowly heated to boiling, whilst the pressure is kept below that of the atmosphere, to prevent leakage. When decomposition is complete, the whole is allowed to cool and the volume of the gas read off. A correction of 1·4 c.c. is added for the solubility of silicon fluoride in sulphuric acid. The results are equal in accuracy to those obtained by Fresenius' method, and the whole determination requires only three hours, of which two are occupied by the cooling. M. J. S.

Air Analysis on a New Principle. By O. Pettersson (*Zeit. anal. Chem.*, **25**, 467—478).—The principle of this method of determining the moisture and carbonic anhydride in atmospheric air consists in performing all the operations in a closed system, in which the influence of barometric variations and changes of temperature is eliminated by adjusting the pressure of the gas undergoing measurement to equality with that of a constant quantity in one part of the apparatus.

The apparatus consists of a pipette with its lower tube graduated, and connected with an adjustable mercury reservoir by a flexible tube. There is a stopcock at its upper end for the introduction of the air for analysis. Below this stopcock are branched in the upper tubes (furnished with stopcocks) two rather larger pipettes filled respectively with phosphoric anhydride and strongly dried soda-lime. The lower tubes of these two pipettes are connected (by stopcock tubes) with the two ends of a sensitive differential manometer, which is a horizontal tube slightly curved and containing as index a drop of coloured sulphuric acid or high-boiling petroleum. The pipettes are all immersed in the same vessel of water. The whole apparatus having been filled with the air for analysis, the mercury having been adjusted to the zero of the graduated stem, and equality of pressure having been established by opening for a moment all the stopcocks, the measured volume of air is compressed into the phosphoric anhydride pipette by admitting mercury until it fills the measuring tube. In 20 minutes all the moisture will have been absorbed. The dried air is re-expanded into the measuring tube; the stopcocks to the manometer are opened, and the level of the mercury is adjusted till the pressure is again equal in all the pipettes. Since the quantity of gas in the soda-lime tube has remained unaltered it serves as a standard volume, although external pressure and temperature may have varied, and the reading of the mercury in the graduated tube at once gives the volume of the aqueous vapour absorbed. The same process is repeated with the soda-lime pipette, in which the carbonic anhydride is absorbed, and now the air in the phosphoric anhydride pipette is employed as the standard volume. M. J. S.

Assay of Iron Pyrites for Sulphur Available for Sulphuric Acid Manufacture. By J. C. Welch (*Analyst*, **11**, 209—213).—In one method, the pyrites is mixed with calcium hydroxide and heated in a tube in a current of oxygen; the contents of the tube are dissolved in hydrochloric acid and boiling water, and precipitated with barium chloride; the presence of lime and iron in solution is perhaps objectionable. The results are only approximate. In the second method, which answers very well indeed, the pyrites is heated in a current of oxygen, the issuing gases are passed through bromine dissolved in hydrochloric acid and water, and the liquid is then boiled and precipitated with barium chloride. The second method is better than the method depending on heating with fuming nitric acid, even in the case of lead sulphide. D. A. L.

Volumetric Determination of Sulphuric Acid. By H. Wilsing (*Zeit. anal. Chem.*, **25**, 560—561).—A measured excess of barium chlorlde is added to the neutral solution, and the excess is then determined by titration with sodium carbonate, using phenolphthaleïn as indicator. The liquid is to be boiled while titrating. Substances precipitable by soda must first be removed. M. J. S.

Volumetric Determination of Sulphates. By H. Quantin (*Chem. News*, **54**, 233—234).—The solution of the sulphate under examination is well mixed with a hydrochloric acid solution of barium chromate to precipitate the sulphuric acid; it is then neutralised with ammonia to remove the excess of barium chromate. The filtrate, containing chromate equivalent to the original sulphate, is acidified with sulphuric acid and titrated with ferrous sulphate, using potassium ferricyanide as indicator. Various necessary precautions are noted. D. A. L.

Determination of Nitric Acid by Absorption of Nitric Oxide in Standard Potassium Permanganate Solution. By H. N. Morse and A. F. Linn (*Amer. Chem. J.*, **8**, 274—280).—The nitric acid is reduced by ferrous chloride and hydrochloric acid in a current of carbonic anhydride. As ordinary marble contains air that cannot be removed by boiling with water, the author uses a saturated solution of sodium hydrogen carbonate containing a quantity of the same salt in suspension. The nitric oxide and carbonic anhydride pass through an empty tube and a set of potash bulbs, the latter containing a strong solution of potassium carbonate to arrest all acid vapours. The washed gases are absorbed in two, long, slanting tubes containing a measured quantity of potassium permanganate. When the absorption is complete, the tubes are emptied and the contents decolorised by dilute sulphuric acid and a measured quantity of oxalic acid, the excess being titrated back with standard permanganate solution; the tubes are cleaned by rinsing with a portion of the sulphuric and oxalic acids. The method yields very accurate and concordant results. H. B.

Lawrence Smith's Plan for Estimating Alkalis in Silicates. By P. Holland (*Chem. News*, **54**, 242—243).—The author's results indicate, firstly, that when carefully performed as directed, practically all the alkali is extracted at one operation; secondly, that the form of crucible recommended by Smith minimises the loss of salts by volatilisation. D. A. L.

Analysis of Silicates. By W. M. Hutchings (*Chem. News*, **54**, 173—174).—The following method is recommended for mineral determinations in silicates. Alkalis are determined by flame colorations, metallic oxides by blowpipe tests, alkaline earths, alumina, and their approximate quantitative relation to one another and to iron by the following method:—A small quantity of the finely-powdered mineral is gently fused with seven times its weight of ammonium fluoride, the fluorides obtained are mixed with sodium carbonate and used in small quantities at a time in a platinum-wire loop before a

very hot flame, the beads are powdered and treated with water, alumina passes into solution, whilst iron and the alkaline earths remain undissolved. A mixture of cuprous iodide and sulphur in connection with the aluminium plate forms a very delicate test for small quantities of bismuth and lead. Both this mixture and Turner's flux keep good for many years. Glycerol is of more general use for boric acid testing than Turner's flux; in presence of copper for example.

D. A. L.

Separation of Zinc from Iron, Cobalt, and Nickel. By P. v. Berg (*Zeit. anal. Chem.*, **25**, 512—519).—Hampe has published (*Chem. Zeit.*, **9**, 543) a process for precipitating zinc from a solution containing the above metals, by converting them into formates and treating with hydrogen sulphide. He, however, found a large quantity of free formic acid necessary to completely prevent the simultaneous precipitation of the other metals. The author shows that by diluting the solution until it contains only about 0·1 per cent. of zinc oxide, a much smaller quantity of formic acid (1 per cent. of 1·2 sp. gr.) ensures a practically complete separation, except in the case of cobalt, which requires a double precipitation.

Monochloracetic acid is still more efficient, a single precipitation being sufficient even with cobalt. To the dilute solution, heated to 50—60°, as much ammonia is added as is equivalent to the zinc present, then a small excess (about 2·6 grams to 450 c.c.) of monochloracetic acid; hydrogen sulphide is then passed slowly through the liquid.

In either case, filtration must be commenced immediately the hydrogen sulphide is in excess, and the precipitate must not be allowed to dry on the sides of the beaker. It is washed with water containing hydrogen sulphide and a little of the organic acid. The test analyses communicated are satisfactory, but the conditions were not varied.

M. J. S.

Aluminium Sulphate containing Aluminium Hydroxide and Free Sulphuric Acid. By H. Hager (*Arch. Pharm.* [3], **24**, 852).—If the neutral sulphate contains any hydroxide, the crystallised salt gives a more or less turbid solution with 2 parts of distilled water. To detect free sulphuric acid, Jorissen's test is applied thus:—A couple of drops of gurjun balsam is warmed with 3 c.c. of acetic acid. About 0·25 gram of the powdered aluminium sulphate is added and warmed gently. In the absence of free sulphuric acid, a whitish or yellowish mixture is formed; in the presence of free acid, a blue coloration appears within a few minutes.

J. T.

Determination of Aluminium in Presence of a Large Proportion of Iron. By R. T. Thomson (*Chem. News*, **54**, 252—253).—The methods depending on boiling with a caustic alkali and subsequent precipitation, or on direct precipitation by sodium thiosulphate, were found to be ineffectual, therefore the following methods of treatment are recommended for getting rid of the great bulk of the iron; the first works best except when much manganese is present, therefore under such circumstances the second method should be used. 1st method:

Reduce the iron to the ferrous state by means of a current of sulphurous anhydride, and boil off the excess, when cool add phosphoric acid or ammonium or sodium phosphate, in excess of that required to precipitate all the alumina, then ammonia until a faint permanent cloudiness is formed, finally excess of ammonium acetate. Should the precipitate contain much iron (it always retains a little), it is washed, redissolved in hydrochloric acid, and again treated with sulphurous anhydride, &c. 2nd method: Add ammonia to the reduced iron solution until a slight cloudiness forms, then excess of ammonium acetate, boil, and if the precipitate contains much iron repeat the reduction and precipitation. In either case, when a satisfactory precipitate is obtained, it is dissolved in hydrochloric acid, boiled with a little nitric acid, nearly neutralised with caustic soda, then boiled with large excess of the last reagent. The alumina is then precipitated as phosphate, the precipitate being washed with a hot 1 per cent. solution of ammonium nitrate, containing about 0·1 gram per litre of ammonium dihydrogen phosphate, and is weighed as $Al_2P_2O_8$. Test results are very satisfactory. The presence of titanium does not interfere with the process. D. A. L.

Silica in the Estimation of Manganese in Pig-iron, and Estimation of Phosphorus in Pig-iron and Steel. By L. M. Deane (*Chem. News*, **54**, 174—175).—When samples of pig-iron containing more than 2 per cent. of silicon are analysed by the ordinary method, an appreciable amount of silica escapes separation, and is finally precipitated with the manganese. The ignited oxide of manganese should therefore be treated with hydrochloric acid, and the silica mixed with it determined in the usual way. For the estimation of phosphorus, the substance is dissolved in nitric acid, evaporated to dryness, redissolved in hydrochloric acid, and again evaporated to dryness. The residue is dissolved in hydrochloric acid, the silica separated, the solution evaporated nearly to dryness, a few drops of nitric acid added, and the heating continued until all nitrous fumes have escaped. The cold solution is mixed with cold water, and the phosphoric acid precipitated and weighed as ammonium phosphomolybdate. D. A. L.

Direct Separation of Manganese from Iron. By L. Blum (*Zeit. anal. Chem.*, **25**, 519—520).—From a solution containing nickel, cobalt, zinc, manganous and ferric chlorides, with tartaric acid and excess of ammonia, potassium ferrocyanide throws down all the metals except the iron. A clear filtrate can be obtained after boiling, but the precipitate cannot be washed. A solution containing 0·00004 gram of manganese and 0·01 gram of ferric chloride per c.c. gives a distinct precipitate. M. J. S.

Detection of Stannic Sulphide in Presence of Antimonious Sulphide. By A. Griffith (*Analyst*, **11**, 164—165).—When a solution containing antimonious sulphide is shaken with ether, and allowed to remain at rest, the sulphide rises to the surface with the ether; stannic sulphide does not behave in this manner. Therefore, when a solution containing both these sulphides is shaken with ether in

sufficient quantity, the antimonious sulphide rises to the surface and exposes the otherwise obscured stannic sulphide. The test does not work with stannous salts. D. A. L.

Production and Measurement of Gold and other Minute Metallic Spheres to Determine their Weight. By G. A. Gozdorf (*Chem. News*, **54**, 231—232).—The minute quantity of pure gold obtained in the assay of very poor ores, &c., is dried on the aluminium plate and taken up by a red-hot boric acid bead in a platinum-wire loop; when heated before the blowpipe the gold is obtained as an almost perfect sphere. The boric acid is dissolved off, and the minute sphere of gold measured under the microscope. A sphere 0·024 mm. diameter = 0·000002178 of a grain of gold has been examined. The modes of calculating are explained. Silver spheres may be obtained and measured in a similar manner; but for copper, lead, and other metals, the boric acid is replaced by sodium carbonate, as the former would dissolve a perceptible amount of these metals. D. A. L.

Estimation of Carbon in the Organic Constituents of Water. By A. Herzfeld (*Ber.*, **19**, 2618—2621).—The method is a modification of that proposed by Degener. The substance is boiled with chromic acid in a flask provided with a reflux condenser, the upper end of which is connected with a chloride of calcium tube. In the middle of the calcium chloride is a layer of powdered antimony, which absorbs any chlorine evolved from the substance. The carbonic anhydride is estimated in an improved form of Rose's apparatus. N. H. M.

Estimation of Nitrates in Water by Means of Aluminium. By S. Harvey (*Analyst*, **11**, 181—186).—The author has adopted the following plan, after considerable experience with the method:—70 c.c. of the water is mixed in a bottle with 30 c.c. of 10 per cent. aqueous soda, a strip of aluminium foil, about 0·75 gram, is put in, the bottle is closed with a stopper carrying an open tube filled with glass beads, and the whole placed under a bell-jar until the reaction (which is aided by warmth) is complete. The contents and washings are made up to a definite volume, and, if possible, Nesslerised directly, otherwise they must be distilled, &c. In cases where free ammonia has to be expelled from the original water, the 70 c.c. is only made slightly alkaline at first, the 30 c.c. of soda being added subsequently. After keeping some time, a reduction in the quantity of ammonia is observed in waters which have not been previously boiled, this is presumedly due to a re-oxidation. Accurate results are obtained. Cane-sugar, or salts of iron, calcium, or magnesium, do not affect the result. Certain sources of error are indicated. D. A. L.

Estimation of Glycerol in Wines. By M. Barth (*Chem. Centr.*, 1886, 504—505).—100 c.c. of wine is concentrated to about 10 c.c., 1 gram of powdered quartz and about 3—4 c.c. of 40 per cent. milk of lime added, and the whole evaporated to dryness. The glycerol is

then extracted with alcohol and finally with ether, the alcohol and ether evaporated on the water-bath, and the glycerol weighed.

L. T. T.

Assay of Carbolic Soap. By A. H. Allen (*Analyst.*, **11**, 103—106).—In the method recommended, the hydrocarbons are removed by agitating the soap, dissolved in soda and water, with ether, and the fatty acids are precipitated by means of brine. An aliquot part of the resulting solution is acidified with sulphuric acid and titrated with bromine-water until the solution is permanently tinged of a faint yellow colour; the bromine-water is standardised immediately before or after use by a solution of phenol or cresol. The remainder of the solution may be used for preparing a larger quantity of the bromine-derivative for qualitative purposes. D. A. L.

Estimation of Invert Sugar. By A. Herzfeld (*Chem. Centr.*, 1886, 603).—In the method described by the author (*Chem. Centr.*, **85**, 604), the time taken in the preliminary heating of the liquid influences the result obtained. The tables given were constructed from experiments wherein this preliminary heating occupied four minutes.

The author recommends the following precautions:—An asbestos plate with a circular opening of 6·5 cm. diameter is placed on the wire gauze, and the flask placed on that, the Bunsen burner being placed at such a height that the flame plays over the whole of the exposed part of the flask, and heats the liquid to boiling in from $3\frac{1}{2}$ to $4\frac{1}{2}$ minutes. With these precautions, the results are very constant. L. T. T.

Titration with Fehling's Solution. By E. Beckmann (*Zeit. anal. Chem.*, **25**, 529—530).—Many persons find a difficulty in recognising the point at which the blue colour disappears. This seems to be due to an optical illusion which causes the colourless liquid to appear complementary in colour to the yellowish-red cuprous oxide. It may to some extent be obviated by adding a drop of zinc chloride, which promotes the separation of the cuprous oxide, but the safest way is to filter and test for copper, which is easily done by placing two thicknesses of filter-paper together, touching one side with the turbid fluid and testing the liquid which soaks through to the other. With diabetic urine, however, it is still necessary to rely on the disappearance of the blue colour. M. J. S.

Detection of Salicylic Acid. By C. O. Curtman (*J. Pharm.* [5], **14**, 523—524).—To 4 c.c. of liquid (wine, beer, &c.) is added 2 c.c. of methyl alcohol, or failing this, the same amount of ethyl alcohol, and then, with care, 2 c.c. of pure sulphuric acid. After mixing, the liquid is heated for about two minutes, allowed to cool for eight or ten minutes, then heated just to boiling, when, if salicylic acid is present, a distinct odour of oil of wintergreen is perceptible. If only traces of acid be present, it may be necessary to allow the liquid to stand, and to heat a third time especially if methyl alcohol has been replaced by ethyl alcohol. Although other ethereal salts are

formed in contact with beer and wine, besides methyl salicylate, the odour of the latter is the most characteristic and the most easily perceived. In examining condensed milk, fats, or other solids and semi-solids, the sample is digested in dilute alcohol at 20—30° for some hours, with frequent agitation. After filtration and concentration, methyl alcohol and sulphuric acid are added as before described; 0·001 part of salicylic acid in a food, &c., can be thus detected.

J. T.

Specific Gravity and some other Characters of Waxes and Allied Substances. By A. H. Allen (*Analyst*, **11**, 223—228).—Methods are described for obtaining fragments of wax, &c., free from air bubbles, for specific gravity determinations; also a method of taking gravities of waxes, &c. (heated by a suitable arrangement to 98—99°), by means of a Westphal balance and glass-rod plummet. The observed gravities indicate that waxes are denser than fats or glycerides in the solid state, but that the reverse is the case with the melted substances. Sperm and bottle-nose oil are shown to be different in composition from spermaceti. Evidence is adduced in support of the glyceride as opposed to the wax-like character of Japan wax (see also next Abstract). The relation of high gravity to high melting point in paraffin is noted.

D. A. L.

Saponification of Fixed Oils. By A. H. Allen (*Analyst*, **11**, 145—147).—The author has collected, grouped, and tabulated results obtained by various investigators in the examination of a large variety of fatty substances by Kœttstorfer's saponification method. Oils consisting of olein mixed with comparatively small quantities of stearin or palmitin, whether of animal or vegetable origin, neutralise about the same quantity of potash—from 18·93 to 19·66 per cent. Oils from cruciferous plants require 17·02 to 17·9 per cent. of potash to neutralise them. Vegetable drying oils require 18·7 to 19·6 per cent. These numbers are not characteristic, but show that linoleic acid must have a higher atomic weight than is generally supposed. With marine animal oils, also, the numbers obtained are not characteristic, varying from 18·51 in cod-liver oil to 21·88 in porpoise oil, which contains much valeric acid; marine waxes, however, require only from 12·30 to 14·74, much less than the marine oils. The butter class contains—butter-fat requiring 22·15 to 23·24, cocoa-nut oil 24·62 to 26·84, palm-nut oil 22·00 to 24·76 per cent. of potash. The various mixtures of palmitin, stearin, and olein require from 19 to 20 per cent. of potash for their neutralisation. Beeswax requires 9·2 to 9·7; Chinese wax 6·5; castor-oil 17·6 to 18·15; Japan wax 21·01 to 22·25.

D. A. L.

Adams' Method for Milk Analysis. By A. H. Allen and W. Chattaway (*Analyst*, **11**, 71—73); and W. Thomson (*ibid.*, 73—75; compare also Abstr., 1886, 583).—Allen rolls up a piece of string with the paper to keep the folds of paper from touching one another; hence ensuring exposure of a more extensive surface. He also ties a cap of filter-paper over the bottom of the coil. With this modified coil, suspended by a loop in the string, 5 c.c. of milk may be run direct from a pipette on to the coil without fear of loss, and then the objec-

tionable two weighings may be dispensed with. Thomson recommends distributing the 5 c.c. of milk on an extended strip of filter-paper, drying quickly, coiling and then extracting the fat in usual manner.

D. A. L.

Separation of Morphine and Strychnine from Fatty Matters. By Focke (*J. Pharm.* [5], **13**, 360—361).—According to the author, the following method gives good results. Exhaust the suspected matter with hot alcohol charged with tartaric acid. Filter after cooling, and evaporate on the water-bath. Take up the residue with 10 times its weight of water and add an excess of baryta-water. After some hours, add a slight excess of sulphuric acid, allow to remain for some time, filter and remove excess of acid by means of barium chloride. Filter and evaporate again so as to completely expel the hydrochloric acid of the barium salt. The residue is taken up with absolute alcohol, and the solution is evaporated to dryness on the water-bath. The new residue, which is slightly acid, is dissolved in water and extracted with ether, which removes the fatty matter taken up by the water. The aqueous solution, after being made alkaline, is again treated with ether, the ethereal solution evaporated, and the residue treated with water acidified with hydrochloric acid, which only dissolves the alkaloïds. J. T.

Detection of Artificial Colouring in Red Wine (Claret). By Samuelson (*Chem. Zeit.*, **10**, 998).—When mixed with an aqueous solution of sodium nitrate, white wine remains clear, but the colour becomes darker. In genuine red wines, a precipitate forms and the supernatant liquid becomes yellow, sometimes only after some time; this is not the case with artificially coloured wines. In a mixture of red and white wines, the amount of precipitate formed is inversely proportional to the quantity of white wine present. White wines coloured red with bilberry, mallow, red poppy, or orseille colouring matter do not give any precipitate. Red wines mixed with coloured white wines yield, in addition to the precipitate, the following reactions: with *bilberry* or *mallow* colours, a violet liquid; with *orseille*, a cherry-red liquid; with *red poppy*, a bright red liquid. The addition of cider to white wine can be detected by sodium nitrate, as cider is coloured dark-brown by this reagent and after some time gives a slight precipitate. D. A. L.

Estimation of Tannin. By H. Dieudonné (*Chem. Zeit.*, **10**, 1067).—This simple and, when carefully conducted, accurate method for estimating tannin is based on reading very small differences of density with a very delicate hydrometer. The hydrometer indicates 1° Baumé, and is divided into hundredths; with this the solution, or extract of the substance to be examined, made with *distilled water*, is tested at 22°, both before and after treatment with powdered skin, the difference in the hydrometric readings is due to tannin. A table is given showing the quantity of tannin corresponding with solutions of densities varying from 1·5 to 105 of the centesimal Baumé degrees at 22°. The standard solutions used in constructing the table con-

tained 0·1 to 10 grams of tannin dissolved in 500 c.c. of water. The ordinary solutions are prepared by boiling and pressing the material four times; they are made up to a definite volume and to a gravity of 1° B. or less, then a measured quantity is shaken with powdered skin, and the next day is filtered, pressed, &c. It is important to use dry and assayed powdered skin as well as good instruments.

D. A. L.

Peptones in the Blood and Urine. By Georges (*J. Pharm.* [5], **13**, 353—354).—All the methods hitherto proposed for the detection of peptones in urine are more or less defective. The author gives the preference to the two following:—

I. This has been recently employed by Wassermann for the detection of peptones in the blood. The blood is received in strong alcohol; the clot thrown on a filter is washed first with cold then with boiling water; the aqueous solution is concentrated to about double the volume of the blood taken, and then added to the alcoholic solution; sodium acetate and ferric chloride are now added to the liquid. After filtration and cooling, the last traces of albumin are removed by adding potassium ferrocyanide and acetic acid, filtered, the excess of ferrocyanide precipitated by copper acetate, filtered, excess of copper removed by hydrogen sulphide; filtered again, and heated on the water-bath to expel hydrogen sulphide and to concentrate the liquid. This method gives good results, especially if care be taken to neutralise, or even to add a slight excess of alkali on adding the sodium acetate and ferric chloride. It also serves very well for the investigation of peptones in urine, commencing by boiling to precipitate albumin coagulable by heat, and terminating as above.

II. The double iodide of potassium and mercury precipitates albumin and the peptones, and Tanret has shown that the albuminous precipitate is insoluble in boiling acetic acid, whilst the peptone precipitate dissolves completely. Employing these reactions, Georges has established a much more rapid method as follows:—Precipitate by heat all the coagulable albumin; treat the urine with acetic acid and the double iodide, wash the precipitate on a filter with cold water charged with acetic acid to the same extent as the urine; wash again with the same acidified water boiling, keeping the washings apart. The clear liquid obtained gives a precipitate on cooling if the least trace of peptonic precipitate has been dissolved. It is only necessary to neutralise in order to obtain a solution to which the double iodide test can be applied.

J. T.

General and Physical Chemistry.

Actinometry. By E. Duclaux (*Compt. rend.*, **103**, 1010—1012).—Oxalic acid in aqueous solution is converted into carbonic anhydride and water by the action of light in presence of oxygen, and this decomposition is not due to any rise of temperature resulting from absorption of the sun's radiation, but is brought about by the visible and ultra-violet rays. In order to secure sufficient contact with the oxygen of the air, the solution is placed in flat vessels and the same volume of liquid is always employed; also, in order to eliminate the somewhat considerable influence of the concentration of the solution, a dilute solution, containing 3 grams of oxalic acid per litre, is employed. The amount of change is determined by titrating with lime-water. If the solution of oxalic acid has been kept for about two months in the dark, it is found to be much more sensitive to the action of light than a freshly prepared solution—a fact which indicates that the two liquids have not the same molecular constitution. The change is analogous to the ripening of collodion. The same degree of sensitiveness can be imparted to a freshly prepared solution by exposing it to sunlight for a few hours, and if a concentrated solution is treated in this way and is then diluted to the strength given, the increased sensitiveness is transmitted to the dilute solutions—a fact which indicates that the alteration takes place in the molecules of the acid and not in those of the water.

The total quantity of acid decomposed when the same quantity of liquid is exposed during the whole day is much greater than the sum of the quantities decomposed when a fresh portion of solution is exposed during each hour, the difference varying from day to day. There is therefore a period of quiescence similar to that which is observed in many photographic and chemical reactions, and which Bunsen and Roscoe have termed photochemical induction in the case of hydrogen and chlorine. C. H. B.

Fluorescences of Manganese and Bismuth. By L. de Boisbaudran (*Compt. rend.*, **103**, 1064—1068).—A mixture of 100 parts of yttrium sulphate with 2 parts of manganese sulphate shows a yellowish-green fluorescence, the spectrum of which consists of a broad band which begins at about 6500, attains its maximum brilliancy at 5640, and fades away gradually at 4890—4840. With 4 per cent. of manganese sulphate, the fluorescence is more intense, but its character is not altered. The fluorescence differs from that of calcium, and is not due to the presence of traces of this element. A mixture of 100 parts of yttrium sulphate with 2 parts of bismuth sulphate gives a red fluorescence, with a spectrum consisting of a band which begins at 6840, attains its maximum brilliancy at 6420—6400, and fades away at 5790—5770. This fluorescence is not due to the presence of magnesium.

Calcium sulphate mixed with small quantities of both bismuth and manganese sulphates gives a fluorescence which is yellow at the centre, and pale-green further from the electrodes. In the spectrum, the orange-red band of the calcium-bismuth fluorescence is very distinct. If the tube is heated, the fluorescence becomes rose-yellow, the red band is scarcely affected, and the brilliancy of the green is diminished. At a higher temperature, the fluorescence diminishes and again becomes green with a bluer shade than originally, and the red band is almost extinguished. In all cases, the fluorescence is much less brilliant than with calcium and manganese sulphates free from bismuth.

A mixture of magnesium sulphate with both manganese and bismuth gives a fluorescence due to the superposition of the magnesium-manganese and the magnesium-bismuth fluorescences.

Cadmium sulphate with small quantities of both manganese and bismuth gives the cadmium-manganese fluorescence, which is somewhat less brilliant than in the absence of bismuth. Strontium sulphate, on the other hand, under similar conditions, gives the strontium-bismuth fluorescence, the intensity of which is somewhat diminished by the presence of manganese.

A mixture of calcium oxide with small quantities of manganese and bismuth oxides gives the calcium-manganese fluorescence with somewhat diminished intensity.

A mixture of zinc and calcium sulphates, in varying proportions, with small quantities of manganese, gives a fluorescence in which the calcium-manganese fluorescence is much more prominent than that due to zinc-manganese. With only 5 per cent. of calcium sulphate, the effect of its presence is readily observed, and it is quite distinct with even 2 per cent. if the tube is heated. C. H. B.

Effect of Manganese on the Phosphorescence of Calcium Carbonate. By E. Becquerel (*Compt. rend.*, **103**, 1098—1101).—The most highly phosphorescent crystals of Iceland spar, which show an orange phosphorescence, contain a somewhat high proportion of manganese, probably in the form of carbonate, with mere traces of iron. The less strongly phosphorescent varieties contain very little manganese.

Calcium carbonate, precipitated from a solution of calcium chloride containing 4 per cent. of manganese chloride, gives almost identical results. Calcium carbonate, formed on the surface of such a solution when exposed in an atmosphere charged with the vapour of ammonium carbonate, does not show the same phenomenon.

These results explain the author's earlier observation, that calcium carbonate precipitated from calcium chloride prepared from Iceland spar, always gives an orange phosphorescence, whilst that prepared from aragonite shows a green phosphorescence. Further experiments are necessary to determine whether manganese is the sole cause of the phenomenon.

The phosphorescence of Iceland spar is affected by lithium, bismuth, and antimony, and by various metallic sulphides.

C. H. B.

Red Fluorescence of Alumina. By L. de Boisbaudran (*Compt. rend.*, **103**, 1107).—Pure calcined alumina shows no red fluorescence when subjected to the action of the silent discharge in a vacuum, but the red fluorescence described by Becquerel ("La Lumière") is shown brilliantly if the alumina contains a small quantity of chromic oxide, and is visible even with so small a proportion as 0·001 per cent.

Alumina with 1 per cent. of manganese oxide shows a green fluorescence; with 1 per cent. of bismuth oxide, a lilac fluorescence in the cold, which becomes blue on heating. Magnesia with 1 per cent. of chromic oxide shows a red fluorescence, whilst the fluorescence of lime containing chromic oxide differs very slightly from that of pure lime. C. H. B.

Phosphorescence of Alumina. By E. Becquerel (*Compt. rend.*, **103**, 1224—1227).—The alumina prepared by Boisbaudran (preceding Abstract) does actually show a feeble red phosphorescence, but after being heated to a very high temperature in a platinum crucible for 15 minutes, it shows the red phosphorescence brilliantly. It would seem, therefore, that Boisbaudran had not sufficiently dehydrated his product.

The author has repeated his earlier experiments, and confirms his former conclusion that pure alumina shows some phosphorescence, which is often greenish in colour, but if strongly heated it shows a brilliant red phosphorescence, the intensity of which is increased by the presence of small quantities of chromium and certain other substances. He points out that the exact character of a phosphorescence or fluorescence will depend on the agent by which the substance is excited and the conditions under which excitation takes place.

C. H. B.

Molecular Refraction of Liquid Organic Compounds of High Dispersive Power. By J. W. Brühl (*Annalen*, **235**, 1—106; see also *Ber.*, **19**, 2746).—In previous papers (Abstr., 1880, 293, 295, 685, 781; 1881, 15; 1882, 263, 445, 827, 829), the author has shown that the mode of union of atoms in a compound, independently of their mere number, has a special influence in raising the molecular refractive power. The present paper embodies a number of new and confirmatory observations, together with discussions of the validity of the several expressions for molecular refractive power, and of the possible connection between dispersion and refractive index or chemical constitution. Numerous references to the work of other physicists are given. The methods of investigation have been previously described.

The first part of the paper contains an account of the preparation and purification of 21 unsaturated compounds specially examined, together with determinations of their densities, refractive indices for the lines α, D, β, and γ, their molecular refractive powers according to Dale and Gladstone's formula $(\mu_\alpha - 1).\frac{P}{d}$, and the more recent or "new" formula $\left(\frac{\mu_\alpha^2 - 1}{\mu_\alpha^2 + 2}\right).\frac{P}{d}$, &c. The constants for these and

for 21 other unsaturated compounds previously examined are arranged in four tables, from which subsidiary tables are constructed to illustrate special points.

Gladstone and Dale's constant was found to be correct within moderate limits of temperature, and since it was applied chiefly to the saturated and feebly dispersive compounds of the fatty series, comparable results were obtained. More recently, H. A. Lorenz (*Ann. Phys. Chem.* [2], **9**, 641) and L. Lorenz (*ibid.*, **11**, 70) have proved by independent theoretical methods that the relation between the velocity of propagation of light and the density of the medium is contained in the formula $\frac{n^2 - 1}{(n^2 + 2)d}$ = constant, when n = refractive index, d = density. This constant was proved by these authors, and by Nasini and Bernheimer, to vary much less with the temperature than the old one. Landolt, also (Abstr., 1882, 909), by its aid has recalculated the molecular refractive powers of many compounds examined by various authors, and found not only that all the earlier established relations are equally well expressed, but that a closer agreement between theory and observation is attained by its use. There still remain, however, serious discrepancies between theory and experiment, especially in the case of substances of high dispersive power.

The question then presented itself: Is there any relation between dispersion and mean refractive index on the one hand, or chemical constitution on the other?

Dispersion may be measured either as $\mu_\gamma - \mu_a$, or by the constant B in Cauchy's equation—

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots$$

(using only constants A and B), in which μ = refractive index for wave-length λ, A = refractive index for infinite wave-length. In the saturated compounds of the fatty series, B is small (0·3 to 0·5); but in the unsaturated compounds tabulated in this paper B is very great, in the case of cinnamaldehyde reaching the enormous value 2·5. Calculating the constants A and B from observations of μ_a and μ_γ, the author has applied Cauchy's equation to calculating μ_D for the last-named substances, and he shows by a tabular statement that theory and experiment agree well for compounds of low dispersion, but that very serious discrepancies arise when the dispersive power is high. Cauchy's equation is therefore untrustworthy in these cases. No definite relation can be traced between dispersion and mean refractive index. (See also following Abstract.) Neither does any connection exist between dispersion and chemical constitution. This is shown by selected examples, in which $\frac{B}{d_4^{20}}$ (dispersion at 20° for unit density) is seen to have very different values for compounds of analogous constitution, nearly equal density and equal refractive index; whilst, on the other hand, the dispersion may be the same for substances of very different chemical structure.

Enquiry is next made into the validity of the old and new formulæ.

Tables are given of the values of $(\mu_a - 1)\frac{P}{d}$ and $\frac{\mu_a^2 - 1}{\mu_a^2 + 2} \cdot \frac{P}{d}$ for the 42 substances, both experimental and calculated by the aid of the following table of atomic refractive powers:—

		r_a.	r_A.	r'_a.	r'_A.
Singly-linked carbon	C′	5·00	4·86	2·48	2·43
Hydrogen	H	1·30	1·29	1·04	1·02
Singly-linked oxygen	O′	2·80	2·71	1·58	1·56
Aldehydic oxygen	O″	3·40	3·29	2·34	2·29
Chlorine	Cl	9·87	9·63	6·02	5·89
Bromine	Br	15·39	14·81	8·95	8·70
Iodine	I	24·69	23·35	13·99	13·36
Singly-linked nitrogen	N′	5·75	5·35	3·02	2·87
Equivalent of ethylene grouping	=	2·30	2·00	1·78	1·59
Equivalent of acetylene grouping	≡	1·90	1·80	1·97	1·86

In this table r_a and r_A are the equivalents for the refractive index of α (red hydrogen line), and A, index for infinite wave-length, using the *old* (Gladstone's) formula: r'_a and r'_A the similar equivalents for the new (Lorenz). This table has been calculated in part by the author, in part by Landolt.

From this table, it is seen that when the molecular refractive power is calculated by the old formula, the differences between theory and experiment in most cases exceed the possible limits of experimental error, and are especially great for substances of high dispersive power. Since all the differences are positive, it is evident that dispersion here tends to raise the molecular refractive power. When the latter is calculated by the new formula, the differences, although still positive, are both relatively and absolutely smaller. The disagreement is, however, well marked in the case of highly dispersive compounds.

To show the disturbing influence of dispersion more clearly, the author in a new table arranges the various substances in the order of ascending values of B (dispersion-coefficient), placing opposite each the differences between the observed and calculated refractions according to the old and new formulæ. When B is small, the discrepancies are relatively about the same for both; but as B increases, there is a rapidly growing inequality between them, the advantage being always with the new formula. The two formulæ are therefore of nearly equal value (as Landolt supposed them always to be) only for feebly dispersive substances. Yet even here the new gives the more concordant results, as the author shows by a new table, including only unsaturated but feebly dispersive compounds.

In the author's opinion, the defects of the new formula are mainly, but not altogether, traceable to dispersion. The general connection between them has been proved above; but it is pointed out that no arithmetical relation exists between the discrepancies and the dispersion-coefficient.

Although as a rule the dispersion is high in compounds containing many C=C groups, some unsaturated compounds of low dispersive power exist. Certain striking examples are mentioned, for which the new formula nevertheless gives good results. These show also that there is no connection between dispersive power and chemical constitution.

Some little space is devoted to refuting Gladstone's theory (Abstr., 1882, 133), adopted by Nasini, namely, that the atomic refraction of carbon-atoms, which are united only to other unsaturated atoms, is higher than that of unsaturated atoms, which are not so united. Examples are given of compounds containing atoms of this kind, for which theory and experiment give concordant results. Moreover, there is no connection between dispersion and such atoms, as proved by the high dispersive power of many substances (aldehyde, furfuraldehyde, &c.) from which they are absent.

The highly important relationship of molecular refractive power to unsaturated carbon groups is next discussed. This has been denied by Nasini and others. (See also Thomsen, following Abstract.) The author rehearses the older arguments on which his views rest, and quotes three series of substances containing 1, 2, and 3 ethylene (C=C) groupings respectively. For these the mean excesses of observed molecular refractive power over that calculated for the empirical formulæ alone, are 1·79, 3·47, and 5·38 respectively. A fourth table shows the empirical refractive powers for a series of seven substances, each containing 4 C=C groupings. In this, the discrepancies range from $4 \times 1{\cdot}73$ for the feebly dispersive allyl phenoxide, to $4 \times 2{\cdot}03$ for the highly dispersive cinnamic alcohol.

It is remarkable that when hydrogen is removed from a hydrocarbon, so as to form a *ring* of singly-linked carbon-atoms, there is no undue increase in refractive power. For example, in *citrene*, *pinene*, and tetrahydroterpene, which according to Wallach contain 2, 1, and 0 C=C groupings, whilst all three contain rings, the excess of observed over empirical molecular refractive power amounts to $2 \times 1{\cdot}78$, $1 \times 1{\cdot}78$ and 0.

In a note, it is pointed out that these considerations speak strongly in favour of Kekulé's benzene formula, as opposed to the prismatic formulæ of Ladenburg and others. Thomsen's thermochemical researches (Abstr., 1880, 785; 1882, 721) lead to exactly opposite conclusions.

The final conclusion of this chapter is: that ethylene groups are effective in raising the molecular refractive power; and that where the increase is greater that can be thus accounted for, it is attributable to dispersion.

A question of practical importance is: how far may the molecular refractive power according to the new formula be safely applied to determining chemical *structure?* This is attacked by making a comparison between the observed and calculated (taking *structure* into account) powers for various substances, and the number of C=C groupings in their molecules. The value of this grouping according to Landolt $=1{\cdot}78$; or rather the mean value, since it is not the same for all series. Many of the slighter discrepancies in the table

may be explained by this variability, the presence of impurities, or uncertainty as to chemical constitution. But of the 42 cases quoted, in only eight does the discrepancy amount to more than the value of an ethylene group; and all these are of substances of high dispersive power. Of the remainder, in only three does the discrepancy equal one-half of 1·78. In some cases even of highly dispersive bodies the difference is less than this. It is not possible to assign an exact limit beyond which dispersion becomes of importance; but, generally, conclusions as to chemical structure are insecure when the dispersion equals that of cinnamic alcohol ($\mu_\beta - \mu_\alpha = 0{\cdot}0248$; $\mu_\gamma - \mu_\alpha = 0{\cdot}0412$; B = 1·38). In such a case efforts should be made to prepare less dispersive derivatives of the substance in question, which is very frequently possible.

In another chapter, the value of the acetylene, C≡C, grouping is discussed. A strong point in favour of the new formula is that here its value is *greater* than that of the ethylene grouping, whereas for the old formula it is *less*. But old and new values are to some extent variable with the dispersion. A fresh study of five compounds (three propargyl-derivatives, heptidene, and acetenylbenzene) leads to the slightly increased mean value (see table above) 2·18. This and the value of the ethylene grouping agree remarkably well with those calculated by the author from Mascart's determinations of μ_D for gaseous ethylene and acetylene (*Compt. rend.*, **86**, 1182).

In Section III, the question is discussed to what extent are the discrepancies between theory and experiment removed by substituting for μ_α in the new formula, the refractive index A for infinite wavelength calculated from Cauchy's formula, using firstly two, and secondly three, constants. An elaborate study of the results so obtained leads to the following general conclusions.

When A is calculated from Cauchy's equation with two constants (A and B), the molecular refractive powers, although in better agreement with experiment, seldom differ much from, and always in the same sense as, those calculated from μ_α. For feebly dispersive substances, in fact, little is gained by the substitution; but for compounds of high dispersive power the advantage is usually, but not always, very decided.

The values of A deduced from Cauchy's equation with two and with three terms are about the same when the disperson is low. But for highly dispersive substances the values of A from the three-termed formula are always the greater; hence the molecular refractive powers calculated from them diverge still more from the observed powers. Here, in fact, the uses of A and of μ_α lead to about the same results.

The author's conclusion is that Cauchy's formula is purely empirical, and without any physical significance. (See also next Abstract.) CH. B.

Experimental Examination of the Older and More Recent Dispersion-formulæ. By J. W. BRÜHL (*Ber.*, **19**, 2821).—The author has shown (preceding Abstract) that in calculating refractive power, the difficulty introduced by dispersion cannot be removed by

substituting for n (the refractive index for any particular wave-length) its value for a wave-length supposed infinite, deduced from Cauchy's well-known equation. In view of the great importance of the subject in its chemical aspect, the author here presents a critical inquiry into the trustworthiness of the various formulæ connecting refractive index with wave-length, which have been proposed from time to time.

Cauchy's original formula, $n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots\ldots$, as well as later modifications of it, lead to the conclusion that the refractive index n diminishes constantly as the wave-length increases, reaching a definite minimum value when λ becomes infinite, a conclusion which is manifestly untrue in the case of substances showing abnormal dispersion. Of the more modern theories discussed, which embrace the phenomena of abnormal dispersion, only one, that of Lommel, implies a limiting value of n greater than unity. Others either do not give such a limiting value (Ketteler's), or give it only under special conditions (Helmholtz's).

In 1879, Mouton proved the untrustworthiness of Cauchy's formula in calculating the dispersion of the ultra-red rays of the spectrum of a specimen of heavy flint glass, when the constants A, B, C, were deduced from the observed values of n for the seven principal Fraunhofer lines. The differences of the observed from the calculated values of n ranged from 0·0023 for $\lambda = 8{\cdot}8$ to 0·0137 for $\lambda = 21{\cdot}4$, amounts which greatly exceed possible experimental errors. Very similar differences existed between the observed values of n for the ultra-red rays of the ordinary and extraordinary spectra of quartz, and the values calculated by Briot's equation $\frac{1}{n^2} = a + b\frac{n^2}{\lambda^2} + c\frac{n^4}{\lambda^4} + \ldots\ldots$ which gives a limiting value of $n = \sqrt{\frac{1}{a}}$ for $\lambda = \infty$. The constants here were calculated from some measurements by Mascart for the lines C, G, O. The results of these experiments are arranged by the author in tabular form, and prove that Cauchy's formula fails when used for calculating by extrapolation the refractive index for ultra-red rays, and *à fortiori* for rays of infinite wave-length. The same is true of Christoffel's modification of Cauchy's equation. All, however, are available for interpolation.

It might be supposed that the failure of Cauchy's formula in these cases was due to the narrow range of observations from which the constants were determined. The author has therefore made a comparison, based on a series of measurements by Langley, between the observed and calculated values of n from the beginning of the ultra-violet to far beyond the red in the spectrum of flint-glass. The constants ($A = 1{\cdot}5504$, $B = 1{\cdot}334171$, $C = -6{\cdot}982411$) were deduced from the values of n for $\lambda = 3{\cdot}97$ (H_1), $\lambda = 7{\cdot}6$, and $\lambda = 18{\cdot}1$ (ultra-red).

The tabulated results are remarkable; in fact Cauchy's formula is here as valueless for interpolation as it was before for extrapolation. The interpolated values in no case agree with the observed values, in

one case differing by so much as 0·0045, whilst the observed values of n for $\lambda = 23{\cdot}56$ (1·5478) and for $\lambda = 28{\cdot}0$ (1·5435) are considerably smaller than the calculated *minimum*, $A = 1{\cdot}5504$ for $\lambda = \infty$. The constant C, too, being negative, it can be shown that n should reach a *maximum* value (= 1·6141) when $\lambda = \sqrt{-\frac{2C}{B}} = 3{\cdot}23$; whilst the observed index for $\lambda = 3{\cdot}44$ was 1·6266, that is, greater than this theoretical maximum.

The author next directs attention to Helmholtz's formula—

$$n^2 - 1 = Q\frac{\lambda^4}{\lambda^2 - \lambda_m^2} - P\lambda^2,$$

in which P, Q, and λ_m^2 depend on the nature of the medium. When $P > Q$, the refractive index must diminish as λ increases, until n^2 becomes negative, that is, until total reflection occurs. When $P = Q$, n reaches a minimum value for $\lambda\ \infty$; but when $P < Q$, this limiting value corresponds with a finite wave-length. A value of n independent of dispersion can only exist, then, when $P = Q$, in which case Helmholtz's formula reduces to Lommel's.

Ketteler's still more recent formula—

$$n^2 - 1 = \frac{A}{\lambda^2 - B} + \frac{C}{\lambda^2 - D} + \ldots$$

gives $n = 1$, when $\lambda = \infty$, that is, the limiting value of n would be unity for all substances, and consequently there could be no index of refraction independent of dispersion.

The author's investigations have now shown that for calculations by interpolation Helmholtz's and Ketteler's equations give equally good results in the case of media of low dispersive power. No choice between them is possible. But when applied to highly dispersive media, Helmholtz's formula is inferior not only to Ketteler's (which contains an additional constant), but also to Cauchy's. Taking a series of measurements of n for oil of cassia (Baden-Powell), the constants for each formula were determined from observations extending to the extreme limits of the visible spectrum. Calculating the values of n for intermediate wave-lengths, the best results were usually obtained by Ketteler's formula. But with constants determined from lines between C and G, Cauchy's formula proved most trustworthy, especially for extrapolation. These conclusions are clearly set forth in a tabular statement.

An important result of this investigation is that Q in Helmholtz's equation is always found > P, which at once disposes of Lommel's theory. The refractive index should therefore be a minimum for some wave-length not infinite. According to the way in which the constants were determined, this minimum was either 1·59 for $\lambda = 8{\cdot}555$, or 1·6002 for $\lambda = 7{\cdot}397$; whereas for the line A, n was observed = 1·5963, or less than the theoretical minimum.

In the foregoing comparisons, the constants were always determined for lines within the limits of the visible spectrum. With constants

determined over a much wider range, Wüllner has found Helmholtz's formula, and Ketteler his own formula, to give excellent results in the case of feebly dispersive substances, although, as the author points out, the two are fundamentally different, and cannot both be correct. From the author's calculations, it appears that both are equally insufficient when applied to highly dispersive media. In proof, a table is given of the differences between the observed values of n for the ordinary and extraordinary spectra of calcspar, and the values calculated by Helmholtz's and Ketteler's equations respectively. The observed values are by Mascart for lines from A to R, and by Sarasin for the ultra-violet (cadmium) spectrum. The constants were determined for lines over the whole spectrum.

The results show that for the extraordinary spectrum, in which the dispersion is low, Helmholtz's formula is satisfactory, Ketteler's somewhat better. But when applied to the ordinary spectrum, in which the dispersion is $2\frac{1}{2}$ times greater, the discrepancies are very serious, extending in the case of Helmholtz's formula to the third place of decimals. Ketteler's equation proved somewhat better.

From his investigations, the author draws the following important conclusions :—That all the formulæ connecting wave-length and refrangibility hitherto proposed are of purely empirical character, and applicable only to media of low dispersive power: that at present it is not certain that the refractive index reaches a limiting value, unity or otherwise, either for $\lambda = \infty$ or for any other wave-length; and, finally, that in investigations bearing on chemical constitution and refractive power, dispersion must either be taken into account, or be eliminated in some empirical way. Ch. B.

Supposed Influence of Multiple Bonds of Union on the Molecular Refraction of the Hydrocarbons. By Julius Thomsen (*Ber.*, **19**, 2837).—In 1862—64, Landolt (*Ann. Phys. Chem.*, **117**, **122**, and **123**) proved beyond doubt that a connection exists between molecular refractive power and chemical composition, by showing that in any homologous series the refractive power increases from member to member by a constant amount, and is independent of isomerism and metamerism.

Since then Brühl (Abstr., 1880, 295, 781; 1882, 445, and preceding Abstract) has endeavoured, with apparent success, to establish a relation between molecular *constitution* and refractive power, by showing that the refractive power of a compound, although independent of the number of single bonds of union between carbon-atoms in its molecule, is decidedly influenced by double and treble bonds. The following considerations, however, make such an influence at least doubtful :—

Brühl's results are summed up in the formula—

$$n \cdot c + 2m \cdot h + \alpha V_1 + \beta V_2 + \gamma V_3 = R \quad . \quad . \quad . \quad . \quad [1]$$

in which R is the molecular refraction of a hydrocarbon C_nH_{2m}, c and h the refractions of a carbon and hydrogen atom respectively, α, β, and γ the numbers of single, double, and treble bonds of union, and

V_1, V_2, and V_3 the increments of refractive power due to them respectively.

Brühl now puts $V_1 = 0$; but this assumption may be avoided, and V_1 eliminated as an independent constant by combining equation [1] with the necessarily true relation $2n - m - \alpha - 2\beta - 3\gamma = 0$. Multiplying the latter by V_1, and adding, we get—

$$n(c + 2V_1) + m(2h - V_1) + \beta(V_2 - 2V_1) + \gamma(V_3 - 3V_1) = R, \quad [3]$$

and finally substituting x, y, p, and q for the constant quantities within brackets, we get—

$$n.x + m.y + \beta.p + \gamma.q = R, \ldots\ldots [4]$$

which is of the same form as [1], and identical with it when $V_1 = 0$, but in which R is not *necessarily* independent of the number of single bonds of union between carbon-atoms. In either case, $x + y = c + 2h + V_1$ represents the increase in refractive power for each addition of CH_2. Experimentally, $x + y$ has been found to vary from 4·85 in the benzene series to 4·525 in the naphthalene-group. No values of x and y can therefore exist which will in all cases satisfy equation [4], and this must also be true of the constants p and q. The following example illustrates this :—

Taking the experimental value of the refraction of two molecules of benzene, $51·86 = 12c + 12h + 6V_1 + 6V_2$, and of one molecule of naphthalene, $43·93 = 10c + 8h + 6V_1 + 5V_2$ and subtracting, we have $2c + 4h + V_2 = 7·93$. From this and the relation $c + 2h + V_1 = 4·85$ or 4·525 we find $V_2 - 2V_1 =$ constant p in equation [4] $= -1·77$ or $-1·12$.

Now Brühl (preceding Abstract) has found the following values for the constants of equation [4] :—

$$x = 2·48, y = 2·08, p = 1·78, q = 1·97 \quad \ldots\ldots [5]$$

The above calculation shows the *negative* influence of p to be as great as Brühl assumes it to be positive.

Again the difference between the molecular refractions of naphthalene and benzene, calculated with Brühl's constants $= 42·02 - 26·46 = 5·56$, whereas the actual difference $= 8·00$. Brühl attributes the discrepancy to the greater dispersive power of naphthalene. The author rather attributes it to the incorrectness of Brühl's hypothesis, which he proceeds to show is unnecessary.

Assuming either that double and treble bonds of union have no influence on molecular refraction, or that $V_2 = 2V_1$, $V_3 = 3V_1$, equation [3] reduces to $R = nx + my$. The author has now determined the constants x and y from the observed molecular refractions of a series of five hydrocarbons of the general formula C_8H_{2m}, containing 1, 2, 3, and 4 double bonds of union, and thus arrives at the equation $R = n \,.\, 4·014 + m \,.\, 0·840$. A table is then given showing the molecular refractions of these five hydrocarbons and of three others, containing from 0 to 5 double bonds, calculated by the author's formula and by equation [4] with Brühl's constants; and the agreement with experiment is seen to be much better in the former case (mean error = 0·37) than in the latter (mean error = 0·8).

The author therefore concludes that the mode of union of carbon-atoms has no influence on molecular refraction.

In the author's formula, the values of x and y can only be regarded as approximate. However, the range of variation is not great. A table is given of the values of x calculated for 22 hydrocarbons, roughly classified according to the number of double bonds in their molecules. Throughout y is taken $= 0{\cdot}84$. In no case does the value of x differ much from the mean value given above. For one group only, of which hexahydronaphthalene may be considered typical, it falls as low as $3{\cdot}75$; but even here $x + y = 4{\cdot}59$ is within the observed limits of variation. CH. B.

Thomsen's Supposed Explanation of Molecular-refraction Relations. By J. W. BRÜHL (*Ber.*, **19**, 3103—3108).—A partial reply to Thomsen (*ibid.*, **19**, 2837, see previous Abstract). The author points out that the constant y in Thomsen's formula for molecular refraction, $R = nx + my$, has been calculated from observations on a series of hydrocarbons of the formula C_8H_{2m}, in which the increments of refractive power for each addition of H_2 are very variable, sometimes positive, sometimes negative, a variability which can only be attributed to chemical constitution. Like other empirical formulæ, Thomsen's is no doubt applicable to the observations from which it was deduced, and possibly to others besides. But in many cases (quoted by the author) it is seriously at fault, whilst the author's formula applies to all hydrocarbons except those having a high dispersive power, to which the author attributes a special influence.

Referring to his previous work (see preceding Abstracts) for a full discussion of the question, he here contents himself with quoting examples of isomeric compounds whose molecular refractive powers differ more or less. In all the compounds selected, the dispersive power is low. Inspection of the table shows that when isomerides are equally saturated, that is, contain the same number of doubly or trebly bound atoms (isovaleric acid, propylic acetate, methylic butyrate), their molecular refractive powers differ very slightly; but when the saturation is unequal (allyl ethyl ether and valeral, cymene and hexahydronaphthalene) the differences are considerable, and beyond the possible limits of experimental error. The influence of saturation on refractive power cannot therefore be ignored. CH. B.

Absolute Electrodynamometer. By H. PELLAT (*Compt. rend.*, **103**, 1189—1190).—A description of a new electrodynamometric balance.

New Apparatus for Electrochemical Investigations. By N. v. KLOBUKOFF (*J. pr. Chem.* [2], **34**, 539—547).—A description, with plates, of a "universal commutator" which fulfils the following conditions:—

That with a given large number of circuits in which the measurement of the strength of the currents has to be determined with one and the same measuring instrument, the making and breaking contact with the latter can be easily and quickly effected.

That the alteration of the strength of a given current caused by throwing the resistance of the measuring instrument out of circuit can be overcome in such a way that at the moment of breaking contact with the measuring instrument, a resistance can be automatically introduced equal to that of the instrument. G. H. M.

Specific Heats and Changes of State at High Temperatures. By Pionchon (*Compt. rend.*, **103**, 1122—1125).

Silver	0—907°	q_0^t =	$0{\cdot}0578t + 0{\cdot}00000044t^2 + 0{\cdot}000000006t^3$.
		γ_t =	$0{\cdot}0578 + 0{\cdot}00000088t + 0{\cdot}000000018t^2$.
	907—1100°	q_0^t =	$0{\cdot}0748t + 17{\cdot}20$.
		γ_t =	$0{\cdot}0748$.
Tin ..	232·7—1110°	q_0^t =	$14{\cdot}375 + 0{\cdot}0612931t - 0{\cdot}000010474t^2 + 0{\cdot}000000010344t^3$.
		γ_t =	$0{\cdot}0612931 - 0{\cdot}000020948t + 0{\cdot}000000310344t^2$.
Iron ..	0—660°	q_0^t =	$0{\cdot}11012t + 0{\cdot}000025333t^2 + 0{\cdot}000000054666t^3$.
		γ_t =	$0{\cdot}11012 + 0{\cdot}000050666t + 0{\cdot}000000163998t^2$.
	660—720°	q_0^t =	$0{\cdot}57803t + 0{\cdot}00143598t^2 + 0{\cdot}000001195t^3$.
		γ_t =	$0{\cdot}57803 + 0{\cdot}00287196t + 0{\cdot}000003585t^2$.
	720—1000°	q_0^t =	$0{\cdot}218t - 39$.
		γ_t =	$0{\cdot}218$.
	1050—1200°	q_0^t =	$0{\cdot}19887t - 23{\cdot}44$.
		γ_t =	$0{\cdot}19887$.
Nickel	0—230°	q_0^t =	$0{\cdot}10836t + 0{\cdot}000022334t^2$.
		γ_t =	$0{\cdot}10836 + 0{\cdot}00004466t$.
	230—400°	q_0^t =	$0{\cdot}183493t - 0{\cdot}000282t^2 + 0{\cdot}000004666t^3$.
		γ_t =	$0{\cdot}183493 - 0{\cdot}00056t + 0{\cdot}000013999998t^2$.
	400—1150°	q_0^t =	$0{\cdot}099t + 0{\cdot}0000375t^2 + 6{\cdot}55$.
		γ_t =	$0{\cdot}099 + 0{\cdot}000061754t$.
Cobalt	0—890°	q_0^t =	$0{\cdot}10584t + 0{\cdot}000022866734t^2 + 0{\cdot}000000021942734t^3$.
		γ_t =	$0{\cdot}10584 + 0{\cdot}000045733t + 0{\cdot}000000065828134t^2$.
	890—1150°	q_0^t =	$0{\cdot}124t + 0{\cdot}00004t^2 - 14{\cdot}8$.
		γ_t =	$0{\cdot}124 + 0{\cdot}00008t$.

Silver affords a further illustration of the identity between the specific heats before and after fusion. Great care was taken to prevent

the absorption of oxygen by the silver, and it was found that under these conditions the metal melts at 907°, a temperature much lower than that given by previous observers.

Molten tin differs from all ordinary liquids in that its specific heat changes very slowly.

Experiments with gas-carbon of which the vessels used to hold some of the metals were made, confirm Weber's statement that at high temperatures the specific heats of the different varieties of carbon are identical.

The variations in the specific heats of the magnetic metals, iron, nickel and cobalt, show that they exist in several allotropic modifications. It is worthy of note that the changes take place at very different temperatures in the three cases. Experiments which are not yet completed, show that these changes of state are intimately connected with the magnetic properties of the three metals.

The author's results confirm Berthelot's criticisim of the law of Dulong and Petit. This law amounts simply to a statement that there is a certain interval of temperature (between 0° and 100°) in which the values of the products of the specific heats of the elements into their combining weights are approximately equal.

C. H. B.

Thermochemistry of Bibasic Phosphates and their Congeners. By A. Joly (*Compt. rend.*, **103**, 1197—1199).—The heats of formation of the bibasic phosphates from the dissolved acids and dissolved oxides were determined both directly and indirectly.

	Cal.
Calcium hydrogen phosphate, $CaHPO_4$, cryst.	+ 26·9
Barium hydrogen phosphate, $BaHPO_4$, gelat.....	+ 26·6
,, ,, ,, ,, cryst.....	+ 27·8
Barium hydrogen arsenate, $BaHAsO_4$, gelat.	+ 27·8
,, ,, ,, ,, cryst.....	+ 28·4
Strontium hydrogen phosphate, $SrHPO_4$, cryst.....	+ 25·2
Manganese hydrogen phosphate, $MnHPO_4$, gelat.....	+ 22·73
Manganese tetrahydrogen phosphate, $MnH_4(PO_4)_2$, gelat.	+ 24·3
Barium hydrogen hypophosphate, $BaH_2(PO_3)_2$, cryst....	+ 35·2
Barium hypophosphate, $BaPO_3$, cryst.....	+ 28·2

The differences between the heats of formation of the colloïdal and crystallised varieties is sufficient to show that the reactions involved in their formation are of a complex character. C. H. B.

Ammonium Magnesium Phosphate. By Berthelot (*Compt. rend.*, **103**, 966—970).—The heat of formation of magnesium ammonium phosphate was determined by measuring the thermal disturbance which takes place when a solution of a magnesium salt is mixed with sodium phosphate and afterwards with ammonia. The numbers thus obtained for the heat of formation of the crystallised double phosphate were +40·7; +41·0; +40·6; +41·9. The last value is probably the most accurate, since the ammonia was added to the crystalline magnesium hydrogen phosphate, and the latter was converted directly into the crystalline double salt. A series of experiments in which a mixture of ammonia and sodium

phosphate was added to the magnesium salt showed that the difference between the heats of formation of the colloïdal and crystalline varieties of the double phosphate is greater than +12·4. These experiments gave a higher value than the first series for the heat of formation of this compound, and the combined results of both series give for the heat of formation of ammonium magnesium phosphate, colloïdal, +29·3 cal.; crystalline, +41·9 cal. These values agree closely with the corresponding values for colloïdal and crystalline trimagnesium phosphate.

When magnesium hydrogen phosphate is in the colloïdal condition, the displacement of the third atom of hydrogen by magnesium develops only +3·7 cal., whilst the same substitution in the crystalline phosphate develops +14·4 cal. Similar phenomena are observed with calcium phosphate. In like manner, the action of ammonia on colloïdal magnesium hydrogen phosphate develops only +4·1 cal., whilst its action on the crystallised salt develops +14·6 cal., a quantity higher than that developed by magnesium, and equal to that developed by sodium or potassium. It follows that ammonium in union with magnesium forms a base, the energy of which is comparable with the energy of sodium and potassium, as already observed in the case of the chlorides and sulphates. (This vol., p. 96.) It also follows that the action of ammonia on trimagnesium phosphate will produce only a very slight thermal disturbance.

Trimagnesium phosphate is rapidly altered by ammonia with production of ammonium magnesium phosphate, not because the heats of formation of the two phosphates for the colloïdal condition are very different, but because the double salt more rapidly passes into the crystalline condition and thus develops heat. This result illustrates the fact that the more or less rapid formation of salts in the colloïdal or crystalline condition depends on the order in which the reacting substances are brought together. Ammonia also acts on crystallised trimagnesium phosphate with development of +0·42 cal., but the reaction is not complete without the addition of ammonium chloride. When this salt is added, there is a slight additional development of heat owing to the formation of a small quantity of magnesium chloride; this fact explains the effect produced by the presence of ammonium chloride when magnesium salts are precipitated by sodium phosphate. This effect is only exerted in presence of at least three equivalents of base. Ammonium chloride alone has no action on magnesium phosphate.

These facts explain the difficulty which is experienced in displacing ammonia from ammonium magnesium phosphate by means of magnesia or lime. Lime tends to produce colloïdal calcium phosphate, the heat of formation of which is less than that of the double phosphate. The heat of formation of crystallised trimagnesium phosphate is also somewhat less than that of the double compound. That decomposition takes place at all is due to the combined effect of the slight dissociation of the ammonium compound in the presence of water, especially if heated, and the volatilisation of the ammonia, which is thus removed from the sphere of action, the magnesium taking its place. C. H. B.

Saturation of Arsenic Acid by Magnesia: Formation of Ammonium Magnesium Arsenate. By C. Blarez (*Comp. rend.*, **103**, 1133—1135).—The developments of heat accompanying the displacement of successive atoms of hydrogen by magnesium are +14·866 cal.; +11·464 cal.; +2·03 cal., giving for the total heat of neutralisation, +28·36 cal.

The heat developed by the neutralisation of arsenic acid by magnesium and ammonium is +37·645 cal., from which it follows that the displacement of the third atom of hydrogen by ammonium develops +11·30 cal. C. H. B.

Heat of Formation of Potassium Methoxide and Ethoxide. By De Forcrand (*Compt. rend.*, **103**, 1263—1266).—Potassium methoxide is obtained by dissolving potassium in excess of anhydrous methyl alcohol and heating the solution in a current of pure dry hydrogen at 200°. Complex alcoholates similar to those formed by sodium are at first formed. The heat of solution at 12° is +11·74 cal.

$CH_3{\cdot}OH$ liq. + $\frac{1}{2}K_2O$ solid = $CH_3{\cdot}OK$ solid + $\frac{1}{2}H_2O$ solid	develops	+ 24·79 cal.
$CH_3{\cdot}OH$ liq. + KHO solid = $CH_3{\cdot}OK$ solid + H_2O solid	„	+ 4·30 „
$CH_3{\cdot}OK$ solid + H_2O liq. = $CH_3{\cdot}OH$ liq. + KHO solid	„	− 2·87 „
$CH_3{\cdot}OH$ liq. + K solid = $CH_3{\cdot}OK$ solid + H gas	„	+ 38·17 „
$CH_3{\cdot}OK$ solid + $n CH_3{\cdot}OH$ liq. = $CH_3{\cdot}OK$ diss. in $n CH_3{\cdot}OH$ liq.	„	+ 12·76 „

Potassium ethoxide is obtained in a precisely similar manner. A small quantity of crystals of the compound EtKO + 3EtOH was obtained. Heat of solution of the ethoxide at 12—15° = +14·70 cal.

$C_2H_5{\cdot}OH$ liq. + $\frac{1}{2}K_2O$ solid = $C_2H_5{\cdot}OK$ solid + $\frac{1}{2}H_2O$ solid	develops	+ 22·28 cal.
$C_2H_5{\cdot}OH$ liq. + KHO solid = $C_2H_5{\cdot}OK$ solid + H_2O solid	„	+ 1·79 „
$C_2H_5{\cdot}OK$ solid + H_2O liq. = $C_2H_5{\cdot}OH$ liq. + KHO solid	„	− 0·36 „
$C_2H_5{\cdot}OH$ liq. + K solid = $C_2H_5{\cdot}OK$ solid + H gas	„	+ 35·66 „
$C_2H_5{\cdot}OK$ solid + $n C_2H_5{\cdot}OH$ liq. = $C_2H_5{\cdot}OK$ diss. in $n C_2H_5{\cdot}OH$ liq.	„	+ 13·59 „

The values for the potassium compounds agree very closely with those obtained previously for the sodium compounds, and the values are practically the same with both ethyl and methyl alcohol. Moreover the values corresponding with the action of potassium and potassium hydroxide on the two alcohols agree closely with those corresponding with their action on water.

In the case of sodium the differences between the heat developed

by its action on the two alcohols respectively, and on water, are much greater than the corresponding differences in the case of potassium, and the absolute values of the quantities are higher with sodium, a result which is due to the fact that the tendency to form polyalcoholic alcoholates is much greater in the case of sodium. Moreover, the heats of formation of the hydrates of potassium hydroxide are much greater than those of the corresponding sodium compounds.

It follows that the alcoholates of potassium ethoxide or methoxide dissolved in the alcohols are practically in the same condition as potassium hydroxide dissolved in water, whilst the dissociation of sodium hydroxide in water is much greater than that of sodium methoxide and ethoxide in the alcohols. C. H. B.

Heats of Neutralisation of Glyceric and Camphoric Acids. By H. Gal and E. Werner (*Compt. rend.*, **103**, 1199—1200).—*Glyceric Acid*, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$.—Heats of neutralisation by the first and second equivalent of potassium hydroxide respectively +11·334 cal. and +12·127 cal.; total +23·461 cal. The addition of a third equivalent of alkali causes no further thermal disturbance.

Camphoric Acid, $C_8H_{14}(COOH)_2$.—Heats of neutralisation by the first, second, and third equivalents of sodium hydroxide respectively, +13·828 cal.; +13·253 cal.; +0·0 cal.; total +27·081 cal.

These results confirm the former conclusion that the total heat of neutralisation of hydroxy-acids is lower than that of acids into which the hydroxyl-group has not been introduced. C. H. B.

Heats of Neutralisation of Malic and Citric Acids and their Pyrogenic Derivatives. By H. Gal and E. Werner (*Compt. rend.*, **103**, 1019—1022).

	Heat of neutralisation.	Heat of solution at about 20°.
Maleic acid	13·310 × 2	— 4·438
Fumaric acid	13·299 × 2	— 5·901
Citraconic acid.....	13·511 × 2	— 2·793
Mesaconic acid.....	13·633 × 2	— 5·943
Itaconic acid.....	12·837 × 2	— 5·923
Malic acid	12·4 × 2	
Citric acid.....	12·8 × 3	

The heat developed by neutralisation is practically the same for each acid function of the same acid.

In all cases, with the exception of itaconic acid, the heat of neutralisation of the pyrogenic derivatives is about 2 cal. greater than that of the generating acid, a relation similar to that already observed in the case of monobasic acids and the corresponding hydroxy-acids (this vol., p. 96). The pyrogenic acids derived from malic acid by the loss of H_2O, and from citric acid by the loss of $CO_2 + H_2O$, no longer contain the hydroxyl-group. C. H. B.

Heat of Neutralisation of Meconic and Mellitic Acids. By H. Gal and E. Werner (*Compt. rend.*, **103**, 1141—1142).—The heat developed by the action of successive equivalents of sodium hydroxide on meconic acid, $OH{\cdot}C_4(COOH)_3$ is + 14·074 cal.; +13·611 cal.; +8·369 cal.; +1·328 cal. = 37·382 cal.

The heat developed by the action of sodium hydroxide on mellitic acid, $C_6(COOH)_6$, is +15·040 cal.; +15·516 cal.; +15·294 cal.; +13·713 cal.; +12·793 cal.; +11·678 cal. = 84·034 cal.

The heat of neutralisation of meconic acid is less than that of mellitic acid, probably because the former is a hydroxy-acid. In both cases the heat of neutralisation diminishes as neutralisation becomes more complete. The values for mellitic acid show that if neutral sodium mellitate is evaporated with excess of hydrochloric acid, it will lose part of the base and yield an acid salt, and the same acid salt will be obtained, when mellitic acid is heated with a solution of an alkaline chloride. The values obtained for mellitic acid are analogous to those found for phosphoric, sulphuric, and other acids in which several hydroxyl-groups are united with the same radicle.

The numbers for the six acid functions of mellitic acid differ more widely than would have been expected from the symmetrical constitution generally assigned to this acid. C. H. B.

Temperature Regulator. By G. W. A. Kahlbaum (*Ber.*, **19**, 2860—2862).—An improvement on Andreæ's form (*Ann. Phys. Chem.* [2], **4**, 164).

Influence of Change of Atmospheric Pressure on Boiling Point. By G. W. A. Kahlbaum (*Ber.*, **19**, 3098—3101).—With the exception of Broch's "Températures d'ébullition de l'eau pure" (*Trav. et Mém. Bureau Internat. des Poids et Mes.*, I., A., **43** (1881)), calculated from Regnault's observations (*Mém. Acad. Sci.*, **21** (1847)), accurate determinations of boiling point at regular intervals of pressure have not been made.

The author has made such a series of measurements for ether (sp. gr. 0·720). The ether was boiled in a platinum vessel, the heating being as uniform as possible; and to avoid possible change of the zero point of the thermometer, the latter was wrapped in wadding and transferred to a vessel of boiling ether after each observation. It was thus maintained at about the same temperature for a period of four months. The author strongly recommends this device. By graphic interpolation, the boiling points were calculated for each mm. of pressure from 721 to 750, and are given in tabular form. Only relative, not absolute, accuracy is claimed for them.

A comparison of this table with Broch's shows that within the ordinary limits of variation of atmospheric pressure, the curves of boiling point for water and ether are practically parallel. Assuming this to be true for other liquids whose boiling point may exceed 100° by as much as that of ether falls below it, the author gives a table of corrections of observed boiling point for each mm. pressure, for liquids boiling between 30° and 170°, of which the following is a condensed form—

Between 720—730 mm.	= + 0·038°	750—760 mm.	= + 0·037°
„ 730—740 „	= + 0·037	760—770 „	= − 0·036
„ 740—750 „	= + 0·037	770—780 „	= − 0·036

or a mean of 1° for each 2·69 mm. This agrees with Kopp's result, 1° = 2·7 mm. (*Annalen*, **34**, 266); Landolt's slightly higher figure, 0·043° = 1 mm. (*Annalen*, Suppl. Bd. **6**, 175), was calculated for lower pressures. Ch. B.

Boiling Points of the Fatty Acids, $C_2H_4O_2$—$C_5H_{10}O_2$. By G. W. A. Kahlbaum (*Ber.*, **19**, 2863—2865).—The author compares his published results with those obtained by Ramsay and Young (Abstr., 1886, 965), and by Richardson (Trans., 1886, 761), and points out their close agreement for pressures varying between 5 and 50 mm. This he regards as sufficient answer to the criticisms of Ramsay and Young. W. P. W.

Vapour-tensions of Ethereal Solutions. By E. Raoult (*Compt. rend.*, **103**, 1125—1127).—The author has carefully measured the vapour-tensions of ethereal solutions of several organic compounds at different temperatures.

Between 0° and 25°, the difference between the vapour-tension of the ethereal solution and that of the ether is exactly proportional to the vapour-tension of pure ether at the particular temperature. For solutions containing from 1 to 5 mols. of the substance in 5000 grams of ether, the difference between the vapour-tension of the solution and that of pure ether is proportional to the amount of solid in solution. The relative diminution of the vapour-tension caused by the solution of 1 gram of the substance in 100 grams of ether depends on the nature of the substance. The molecular reduction of the vapour-tension k is obtained by the formula $k = \frac{f + f'}{f} \times \frac{M}{P}$, in which f is the vapour-tension of ether, f' the vapour-tension of the solution, M the molecular weight of the substance, and P the amount dissolved in 100 grams of ether. It is found that if a gram-molecule of any compound whatever is dissolved in 100 grams of ether, the vapour-tension of the ether is diminished by a constant fraction of its normal value. For all temperatures between 0° and 25°, the value of this fraction is 0·71. C. H. B.

Apparatus for Measuring the Tension of Vapours. By G. W. A. Kahlbaum (*Ber.*, **19**, 2954—2958).—The essential point in this apparatus is the maintenance of a uniform temperature by the circulation of a current of water heated in a vessel exterior to the jacket. W. P. W.

Dissociation of Salts containing Water of Crystallisation. By W. Müller-Erzbach (*Ber.*, **19**, 2874—2876).—A continuation of the author's experiments (Abstr., 1885, 952; 1886, 10) in which the relative vapour-tensions of the water in the salts and of pure water are compared. The following salts are examined: $CaN_2O_6 + 4H_2O$,

relative tension = 0·06—0·07: $CaN_2O_6 + 3H_2O$, relative tension = 0·10—0·11; after the loss of 1 mol. H_2O, this fell to 0·04. The salt obtained by dissolving the latter in a fourth molecular proportion of water had a relative tension = 0·27—0·36; after 2 mols. H_2O had been removed, the tension fell to 0·08—0·07, and reached 0·04 before the last traces of water were removed. The author regards this variation in the tension required to separate the different proportions of the water from the solution as affording good evidence of the existence of a molecular compound in the liquid. With $SrN_2O_6 + 4H_2O$, the relative tension at 12·4° was 0·61; $ZnN_2O_6 + 6H_2O$, relative tension = 0·18 at 12·1°, after the loss of $2H_2O$ this fell to 0·025, and became imperceptible when a salt containing 3 mols. H_2O was left. $BaH_2O_2 + 8H_2O$ lost 1 mol. H_2O with a relative tension = 0·88—0·92, 5 more mols. H_2O were lost when it fell to 0·18—0·22, and a diminution to 0·10 to 0·12 accompanied the separation of a seventh mol. H_2O; 1 mol. H_2O remaining combined with the salt. $SrH_2O_2 + 8H_2O$ lost 1 mol. H_2O with a relative tension = 0·73 at 17·6°, and a further 6 mols. H_2O with a relative tension = 0·27 at 18·5°, 1 mol. H_2O remaining combined with the hydroxide.

W. P. W.

Dissociation of Copper Sulphate. By W. Müller-Erzbach (*Ber.*, **19**, 2877—2879).—In this paper, it is pointed out that H. Lescœur, working with a different method and at higher temperatures, has arrived at results (this vol., p. 100) which agree exactly with those previously obtained by the author (Abstr., 1886, 10). Lescœur, in his criticisms on the author's earlier experiments (Abstr., 1884, 952), has overlooked these more recently published experiments on the dissociation of copper sulphate.

W. P. W.

The Relation between the Efflorescence and Deliquescence of Salts and the Maximum Vapour-tensions of their Saturated Solutions. By H. Lescœur (*Compt. rend.*, **103**, 1260—1263).—The presence of a few tenths of a per cent. of water over and above that which is actually combined with the salt, is sufficient to give the maximum vapour-tension of its saturated solution. In order that a salt may be deliquescent, the maximum vapour-tension of its saturated solution must be lower than that of the aqueous vapour in the atmosphere. The following table gives the vapour-tensions of the saturated solutions, and may be termed the scale of deliquescence at 20°:—

Potassium nitrate	15 mm.	Strontium bromide..	9·1 mm.
Potassium chloride ..	13·55 mm.	Potassium carbonate	6·9 ,,
Sodium acetate (cryst.)	12·4 ,,	Magnesium chloride	5·75 ,,
Iodic acid	11·6 ,,	Calcium chloride ...	5·6 ,,
Strontium chloride....	11·5 ,,	Potassium acetate ..	3·9 ,,
Sodium nitrate	11·15 ,,	Arsenic anhydride..	2·3 ,,
Sodium chromate	10·6 ,,	Sodium hydroxide ..	1·0 ,,
Calcium nitrate	9·3 ,,	Potassium hydroxide	0·8 ,,
Ammonium nitrate ..	9·1 ,,		

On the other hand, if the vapour-tension of a hydrated salt is greater than that of the aqueous vapour in the air, the salt will be efflorescent. The following table furnishes a scale of efflorescence at 20°:—

Sodium arsenate, $Na_2HAsO_4 + 12H_2O$	16·0 mm.
,, sulphate, $Na_2SO_4 + 10H_2O$.....	13·9 ,,
,, phosphate, $Na_2HPO_4 + 12H_2O$.....	13·5 ,,
,, acetate, $NaC_2H_3O_2 + 3H_2O$	12·4 ,,
,, carbonate, $Na_2CO_3 + 10H_2O$.....	12·1 ,,
,, phosphate, $Na_2HPO_4 + 7H_2O$	9·0 ,,
Cupric sulphate, $CuSO_4 + 5H_2O$.....	6·0 ,,
Strontium hydroxide, $SrH_2O_2 + 8H_2O$	5·6 ,,
,, chloride, $SrCl_2 + 6H_2O$	5·6 ,,
Nickel chloride, $NiCl_2 + 6H_2O$	4·6 ,,
Sodium arsenate, $Na_2HAsO_4 + 7H_2O$.....	4 6 ,,
Barium hydroxide, $BaH_2O_2 + 8H_2O$	4·2 ,,
Boric acid, H_3BO_3, about	2·0 ,,
Strontium bromide, $SrBr_2 + 6H_2O$, about.....	1·8 ,,
Oxalic acid, $H_2C_2O_4 + 2H_2O$, about.....	1·3 ,,

C. H. B.

Density of Weak Aqueous Solutions of Certain Salts. By J. G. McGregor (*Chem. News*, **55**, 3—6).—Experiments have been made to decide:—1. Whether or not there are solutions of salts, given volumes of which are less than the volumes of the water they contain. 2. How the density of very weak solutions varies with their strength. Anhydrous copper sulphate has already been shown to form weak solutions exhibiting the first property. Experiments with zinc sulphate, magnesium sulphate, and calcium chloride now show that these salts do not behave in this manner, but that the solutions they form are always of greater volume than the water they contain. The strength of the solutions examined, varied in the case of zinc sulphate from 0·186 to 2·895 per cent. of the salt; of magnesium sulphate from 0·191 to 1·132; of calcium chloride from 0·191 to 1·320 per cent. With regard to the density of the solutions: with the zinc and magnesium salt, the increase in density is nearly in direct proportion to the percentage of salt in solution, whereas with calcium chloride the rate of increase of density with concentration diminishes as the percentage of salt in solution increases. The mode of experimenting is fully described and the results are tabulated. D. A. L.

Cohesion and Submersion Figures. By C. Tomlinson (*Chem. News*, **55**, 1—2).—Referring to a paper by Ackroyd on this subject (Abstr., 1886, 971), the author recalls the work of Rogers and his own work in the same direction. In 1864, he published papers on "Submersion Figures" produced by a large variety of liquids, and diagrams were given illustrating the formation and structure of these liquid "rolling rings," and also of aërial "rolling rings." Reference is also made to other work on the same subject, to the modes of exhibiting vortex rings at the lecture table, and to the author's researches

on the action of nuclei and porous bodies in liberating vapour from boiling liquids. D. A. L.

Weight of Drops and their Relation to the Constants of Capillarity and the Capillary Meniscus Angle. By J. Traube (*J. pr. Chem.* [2], **34**, 515—538; compare this vol., p. 101).—From the results obtained with water and with solutions of alcohol of different strengths, the author concludes that the weight of drops and their capillary constants decrease with the increasing curvature of the surface of formation of the drops; this decrease does not, however, begin before a certain degree of curvature, which is different for different liquids. The decrease of the weight of drops in the case of different liquids is not proportional to the increase of curvature, but appears to be the greater the smaller the capillary constants of the liquid. He also finds that the edge-angle of the meniscus of drops of different liquids is equal or proportional to the meniscus angle of the same liquid in capillary tubes.

The author also made a series of determinations with solutions of alcohols and acids of different strengths, observing in each case the time which was necessary for the formation of a drop from a capillary tube and also the time necessary for the formation of a drop plus the curved surface of its meniscus; by working out the proportion between these, he found that the ratio of the time of formation between the curved surface of the drop-meniscus and the drop increases with the increasing radius of the tube; and that the drop-meniscus in general increases in proportion to the drop with increasing concentration of the solution; that is, with decreasing cohesion. The difference in the quotient $\frac{T_w}{T_t}$ decreases with increasing concentration (T_w = time of formation of the drop-meniscus, T_t = that of the drop); therefore, curves constructed with the concentrations (as abscissæ) and these quotients are concave. With compounds of an homologous series, and equal concentration, the drop-meniscus increases with the molecular weight of the dissolved substance. The determination of the size of the drop-meniscus was made in order to see if any conclusion regarding the meniscus angle could be drawn from their respective sizes. The results showed that—1. The volume of the drop-meniscus and the top meniscus angle, which the tangential planes, formed by the last particles of the curved surface of the drop-meniscus, form with the horizontal tube wall, decreases with increasing concentration of the solution, like the meniscus angle in capillary tubes. 2. For substances of an homologous series, in solutions of equal strength, the volume of the drop-meniscus decreases with the increasing molecular weight of the dissolved substance, as do also the top edge of the angle of the drop-meniscus, and the meniscus in capillary tubes.

In conclusion, the author considers that Laplace's hypothesis, according to which the meniscus angle for wetting liquids is equal to 0, cannot be maintained in view of the results obtained by the direct measurement of the capillary meniscus at different temperatures, and by the measurement of drops; moreover, one of the most important

theories of capillarity can only be maintained if the finiteness of the meniscus angle is accepted.

Wilhelmy's important law of the constancy of the meniscus angle cannot be accepted in its universality, since the size of this angle appears to depend on the temperature of the liquid and the curvature of the walls of the tube. Moreover, the meniscus angle, which the surface of a drop forms with a horizontal glass surface, is not, as Quincke supposes, equal to that which is enclosed by the meniscus surface in tubes with a vertical partition. The one is perhaps the complement of the other. G. H. M.

Volatilisation of Dissolved Substances during the Evaporation of the Solvent. By P. M. Delacharlonny (*Compt. rend.*, **103**, 1128—1129).—Concentrated solutions of sulphuric acid, sodium hydroxide, sodium carbonate, and ferric sulphate were heated at 65—70° in vessels closed by inverted funnels. In a few hours, the fact that some of the dissolved substance had been carried off in the vapour of the solvent was easily recognised by means of suitable test-papers which had been placed in the apex of each funnel. Even at the ordinary temperature, the papers had distinctly changed after four or five days.

Acid solutions of alum and of ferrous sulphate at the ordinary temperature gave similar results.

There is no evidence of the actual carrying off of solid particles; the colour of the test-papers was uniform, and not in streaks or patches. C. H. B.

The Periodic Law. By W. Spring (*Ber.*, **19**, 3092—3093).—A question of priority with regard to Emerson Reynolds's illustration of this law (*Chem. News*, **54**, 1).

Inorganic Chemistry.

Formation of Active Oxygen in the Atmosphere, and its Connection with the Electric Phenomena of the Air and the Production of Storms. By C. Wurster (*Ber.*, **19**, 3208—3217).—Observations made by the author lead him to conclude that ozone is formed in the air by the action of sunlight on clouds. When clouds are continually formed from above, they all become laden with ozone, whilst when they form from below only the upper layer will contain much ozone. In the former case, the accumulation of ozone causes the clouds to become strongly negatively electric, and so gives rise to thunderstorms. N. H. M.

Formation of Active Oxygen in Paper. By C. Wurster (*Ber.*, **19**, 3217—3218).—The yellow and brown colour acquired by some

papers is due to the action of active oxygen on the resin used in sizing the paper, or in some cases on the woody matter present in the paper. By means of dimethylparaphenylenediamine paper (this vol., p. 298), the presence and even the percentage amount of woody matter can be determined in a paper. When the moist dimethylparaphenylenediamine paper is pressed between paper containing wood, it acquires a deep red colour. Ordinary sized paper merely turns it a delicate rose colour. N. H. M.

Phosphorus Pentafluoride. By H. Moissan (*Compt. rend.*, **103**, 1257—1260).—Perfectly dry phosphorus pentafluoride confined over mercury is not decomposed by the action of induction sparks 40 mm. in length, a result which agrees with Thorpe's earlier observation. With sparks 150—200 mm. in length, however, the gas is decomposed into phosphorus trifluoride and fluorine, the latter at once attacking the glass and the mercury.

Phosphorus pentafluoride yields no trifluoride when heated to dull redness with an excess of phosphorus. In this respect, its behaviour differs from that of the pentachloride. It is not affected by sulphur vapour at 440°, nor by iodine vapour at 500°. In presence of a minute trace of water, it attacks glass, with formation of silicon fluoride and phosphorus oxyfluoride, whilst the alkalis in the glass are converted into phosphates or fluorphosphates.

In order to analyse the gas, a measured volume was absorbed in water in a platinum vessel, treated with nitric acid and molybdic solution, and the phosphorus finally weighed as magnesium pyrophosphate. Another method consists in absorbing a measured volume in potassium hydroxide solution, which is mixed with some pure silica, evaporated to dryness, mixed with concentrated sulphuric acid, and heated until vapours of this acid begin to come off. The liquid is then diluted, made alkaline with ammonia, and the phosphorus precipitated as magnesium ammonium phosphate.

The results agree with the formula PF_5; the first method is the most accurate. C. H. B.

Compounds of Selenious and Arsenious Anhydrides with Sulphuric Anhydride: Isolation of Sulphuric Anhydride. By R. Weber (*Ber.*, **19**, 3185—3190).—When selenious anhydride is warmed with very carefully purified sulphuric anhydride, it dissolves therein, and if the excess of sulphuric anhydride is distilled off at 60—70°, a crystalline compound, SeO_2,SO_3, is left. This substance is decomposed by a temperature of 100°, sulphuric anhydride being evolved. Water decomposes it with great violence.

In like manner, sulphuric anhydride dissolves arsenious anhydride. If the excess of sulphuric anhydride is distilled off at 60°, a compound of the formula $As_2O_3,6SO_3$ is left; if the distillation is continued at 100°, the residue has the formula $As_2O_3,3SO_3$. These compounds are quite distinct from the compound As_2O_3,SO_3 discovered by Reich in 1863 in the Freiberg smelting works.

The author states that the specimens of pure sulphuric anhydride previously obtained and described (this Journal, 1877, ii, 164) still

retain their original character, melting and resolidifying at 15°, and showing no signs of forming allotropic modifications. He is still of opinion that the various modifications of sulphuric anhydride are all due to the presence of traces of moisture. He describes further precautions for obtaining absolutely pure anhydride, and considers the best method to be to cohobate carefully purified sulphuric anhydride with phosphoric anhydride in a slight modification of the bent and sealed distilling tube previously described (*loc. cit.*). After continued cohobation, the sulphuric anhydride will remain liquid down to 15°, even in contact with the phosphoric anhydride. Finally the sulphuric anhydride may be distilled over into the opposite end of the distilling tube, and this then sealed off without the air being able to come in contact with the inside of the tube. Phosphoric anhydride forms a compound $P_2O_5,3SO_3$, which crystallises out from the excess of sulphuric anhydride. This compound decomposes at the boiling point of sulphuric anhydride. L. T. T.

Behaviour of Iodine with Realgar and Arsenic Iodosulphide. By R. Schneider (*J. pr. Chem.* [2], **34**, 505—514).—*Arsenious iodosulphide*, AsI_3,As_2S_3, is prepared by heating together either a mixture of realgar (1 mol.) and iodine (2 atoms) with the least possible access of air, or a mixture of 3 parts arsenious iodide with 1·6 parts of arsenic trisulphide. It forms an amorphous, vitreous mass with conchoïdal fracture, and is of a dark red or reddish-brown colour. It is not acted on by the air at ordinary temperatures. When heated at 100°, it softens, and boils at a higher temperature without evolution of iodine vapour, but with partial decomposition into arsenious iodide and sulphide. It is insoluble in hot and cold alcohol, ether, carbon bisulphide, and chloroform. Hot water slowly decomposes it with formation of hydriodic acid. Boiling hydrochloric acid slowly decomposes it with evolution of iodine. When boiled with concentrated sulphuric acid, it gives off iodine, sulphur and sulphurous anhydride. Potassium and ammonium hydroxides dissolve arsenious iodosulphide to a colourless liquid, from which dilute acids precipitate arsenious sulphide, whilst the whole of the iodine and part of the arsenic remain in solution. When treated with an ammoniacal solution of silver nitrate, it is decomposed, forming silver iodide, sulphide, and arsenite. This reaction affords a means of determining the composition of the substance.

When realgar is shaken with a solution of iodine in carbon bisulphide, and iodine is added in small quantities until the whole of the realgar is dissolved (1 mol. realgar requires 6 atoms iodine), and the solution then evaporated, arsenious iodide separates, partly in hexagonal plates and partly in rhombohedrons, mixed with long prisms of sulphur. Also, when a mixture of realgar (1 mol.) with iodine (6 atoms) is heated, and the resulting mass is dissolved in carbon bisulphide, arsenious iodide and sulphur are formed.

G. H. M.

Arsenic Pentasulphide. By L. W. McCay (*Chem. News*, **54**, 287).—When a solution of an alkaline arsenate strongly acidified with hydrochloric acid and saturated with hydrogen sulphide is

heated in a closed vessel at 100° for one hour, the arsenate is completely converted into pentasulphide. It contains no trisulphide, and if due precautions have been taken to exclude air, no free sulphur. Pure arsenic pentasulphide is lemon-yellow in colour, does not yield any sulphur to carbon bisulphide, and dissolves in ammonia without separation of sulphur. When the ammoniacal solution is agitated with silver nitrate and filtered, a clear filtrate is obtained, from which nitric acid precipitates silver arsenate. The formation of arsenic pentasulphide in this manner confirms Bunsen's results, he having obtained it by the action of hydrogen sulphide on hot solutions of arsenic compounds. D. A. L.

Carbonic Anhydride in the Atmosphere. By R. Blochmann (*Annalen*, **237**, 39—90).—The author gives an account of the various methods which have been used for the estimation of the carbonic anhydride in the atmosphere from the time of Saussure to the present day. It is pointed out that Pettenkofer's method yields too high results; the normal amount of carbonic anhydride in 10,000 volumes of air is 3, not 4 volumes. The author describes a modification of Pettenkofer's method, which permits of the baryta-water being filtered through asbestos and titrated without coming into contact with the air of the atmosphere. A double burette of special construction is required. Drawings of the apparatus are given in the original. W. C. W.

Bimetallic Phosphates. By A. Joly (*Compt. rend.*, **103**, 1129—1132).—The action of disodium hydrogen phosphate on solutions of metallic salts varies with the conditions, and with the nature of the metal. In some cases, with silver nitrate for instance, an amorphous precipitate of the tribasic phosphate is at once produced; in others, a gelatinous monophosphate is at first precipitated, and this gradually passes into a crystalline diphosphate. In the case of the alkaline earths and manganese, the first stage in the reaction is represented by the equation $4Na_2HPO_4 + 4M''Cl_2 = M_3''(PO_4)_2 + M''H_4(PO_4)_2 + 8NaCl$.

The monophosphates decompose in presence of water with a rapidity which depends on the nature of the metal and the concentration of the solution (Abstr., 1884, 556).

In some cases, there is an intermediate reaction, the gelatinous monophosphate becoming crystalline. This is the final stage of the reaction if the conditions are such as to prevent the formation of a diphosphate. The diphosphates decompose at 100° into crystalline tribasic phosphates and the free acid, and at the ordinary temperature the reverse change takes place to a greater or less extent. These facts indicate that the intermediate phosphates described by various authors are in reality mixtures. The precipitation of silver phosphate may be regarded as taking place in two stages, the first products being the trisilver phosphate and the monophosphate, the latter immediately decomposing into the tribasic salt and the free acid, which limits the extent of the reaction. The formation of disilver phosphate is impossible under these conditions, since this salt is immediately decomposed by water (this vol., p. 215).

In the case of hypophosphoric acid, the precipitate is at first a gelatinous bibasic phosphate, which rapidly changes into a crystalline monobasic phosphate (Abstr., 1886, 200, 408, 593, 662).

C. H. B.

Silver Phosphates and Arsenates. By A. Joly (*Compt. rend.*, **103**, 1071—1074).—Precipitated and amorphous silver phosphate dissolve in phosphoric acid solution, the solubility increasing with the concentration of the acid and the temperature. If a liquid containing less than 38 parts of phosphoric anhydride to 100 parts of water is saturated with silver phosphate at 80° and allowed to cool, it deposits trisilver phosphate in pale-yellow, rhombic dodecahedrons modified by faces of the icositetrahedron. The mother-liquor deposits no more crystals on standing, but will dissolve a further quantity of amorphous silver phosphate if heated, and thus the same solution of phosphoric acid can be used for the crystallisation of an unlimited quantity of silver phosphate.

If the solution contains 40 parts of phosphoric anhydride to 100 parts of water, it deposits disilver hydrogen phosphate, Ag_2HPO_4, in colourless crystals derived from a hexagonal prism. They generally form long prisms with rhombohedral terminations. In contact with water or alcohol, they become yellow, and decompose into trisilver phosphate and phosphoric acid, but they are not affected by ether. If the concentration of the phosphoric acid solution differs much from the strength given, the product is a mixture of crystals very difficult to purify.

When the crystals of disilver hydrogen phosphate are heated to 110—150°, they yield silver pyrophosphate, $Ag_4P_2O_7$, which can also be obtained by heating the syrupy solution of the silver phosphate to the same temperature. Hurtzig and Geuther obtained the same compound by adding ether to the solution which had been heated. The pyrophosphate is not, however, formed in the wet way as these authors supposed, since under the given conditions of concentration, the fused acid salt, and not its solution, is decomposed. The experiment simply shows that disilver hydrogen phosphate yields the pyrophosphate at a lower temperature than that at which phosphoric acid is converted into pyrophosphoric acid.

Silver arsenate is much less soluble than the phosphate in the free acid. If the solution contains less than 70 parts of arsenic anhydride to 100 parts of water, the solution saturated with amorphous silver arsenate at 80° deposits very brilliant, black, opaque crystals of trisilver arsenate, which are unmodified rhombic dodecahedra.

A solution of arsenic acid of the composition $H_3AsO_4 + H_2O$, when saturated with silver arsenate, yields white monoclinic crystals of silver dihydrogen arsenate, a compound which is very readily prepared. It is decomposed into trisilver arsenate and arsenic acid by a trace of water, and if heated to 100° yields silver metarsenate in the form of a white powder which absorbs water very slowly. Before losing water, the crystals of the acid salt become red, probably owing to the formation of arsenic acid and disilver hydrogen arsenate, Ag_2HAsO_4. In fact, if a solution from which silver dihydrogen arsenate will crystallise is saturated with silver arsenate at a tempera-

ture a little below 100°, it deposits orange-red hexagonal prisms with rhombohedral terminations. Their form agrees with that of disilver hydrogen phosphate, and indicates that they are disilver arsenate, but they could not be purified.

When a syrupy solution of silver arsenate in arsenic acid is heated above 100°, it yields a white granular powder similar in appearance to the compound $Ag_2O,2As_2O_5$, described by Hurtzig and Geuther.

C. H. B.

Solubility of Silver Chromate in Ammonium Nitrate. By R. F. Carpenter (*J. Soc. Chem. Ind.*, **5**, 286).—It is found that on treating freshly precipitated silver chromate with a strong solution of ammonium nitrate, the solution instantly assumes a bright yellow colour in the cold. On warming, the rate of solution rapidly increases up to the boiling point; on cooling, the silver chromate crystallises out in needle-shaped crystals. In a paper by G. Biscaro (*Chem. News*, **53**, 67) "On a Defect in the Volumetric Estimation of Chlorine by Mohr's Process," it was stated that "if nitrates, especially those of the alkalis and alkaline earths, are simultaneously present, the precipitation of the red silver chromate often takes place too late," a circumstance which the author considers to be fully explained by the above experiments. The subjoined table gives the results of some experiments made to determine the relative solubility of silver chromate in the nitrates of potassium, sodium, ammonium, and magnesium in cold and hot strong solutions:—

	One-tenth normal silver nitrate added.		Grains of silver chromate dissolved in hot solution.
	10°.	100°.	
Pure water.....	0·05 c.c.	0·25 c.c.	0·064
Sodium nitrate	0·05 „	0·25 „	0·064
Potassium nitrate ..	0·10 „	0·75 „	0·192
Ammonium nitrate.	0·07 „	1·25 „	0·320
Magnesium nitrate..	0·35 „	1·00 „	0·256

50 grains of each of the above salts were dissolved in 100 c.c. of water, and the amount of decinormal silver nitrate solution taken to obtain the reaction with potassium chromate is given in the table. In the last three cases, the author has deducted the amount of silver chromate dissolved by the water alone, and has given the amount due to the solvent action of the respective nitrates. From all these, the silver chromate crystallised out again on cooling. D. B.

Tetracalcium Phosphate and Basic Converter Slag. By E. Jensch (*Ber.*, **19**, 3093—3101).—It has been generally assumed that the phosphoric acid in basic converter slag is present as tetracalcium phosphate. The author has endeavoured to prepare such a phosphate by heating tricalcium phosphate with calcium carbonate to a high temperature. He has failed to obtain a crystalline substance such as is frequently seen in the basic slag, but at the same time the properties of the tricalcium phosphate are so altered as to indicate some chemical change having occurred.

The following analyses of basic slag are quoted:—I. Mean results

for the slag of all German works (Hasenclever). II. Mean of 12 analyses of slag from the steel works at Friedenshütte. III. Mean of four analyses of slag from Witkowitz.

	P_2O_5.	CaO.	MgO.	FeO.	Fe_2O_3.	Al_2O_3.	MnO.	S.	SO_3.	SiO_2.
I.	17·25	48·29	4·89	9·44	3·78	2·04	3·91	0·49	0·22	7·96
II.	18·93	54·87	4·90	8·83	5·20	3·51	0·51	0·44	—	6·85
III.	16·86	49·45	1·26	9·88	5·96	2·17	2·93	0·61	0·10	10·08

The author considers that II may be regarded as consisting of—

P_2O_5,4CaO.	Mn_2O_3,3CaO.	Fe_2O_3,3CaO.	SiO_2,2CaO.	CaS.
48·78	1·20	30·77	19·59	0·99

With regard to the statement frequently made, that a large proportion of the phosphorus is present in the form of iron phosphide, the author's results show that at most only 1·5 per cent. can be present in this form, and that even this is rendered soluble in the soil.

A. J. G.

The Determination of Water in the Hydrates of Strontium Oxide. By C. Scheibler (*Ber.*, **19**, 2865—2868).—A controversial paper, in which the author rejects the deduction drawn by C. Heyer (this vol., p. 108), as evidence of the existence of a dihydrate of strontium oxide. It is also pointed out that Heyer's method for the determination of water in the dihydrate has only a limited value, since it is inapplicable to the monohydrates of the alkaline earths and to the dihydrate of barium oxide. W. P. W.

Action of Carbonic Anhydride on the Dihydrate of Strontium Oxide. By R. Finkener (*Ber.*, **19**, 2958—2963).—The author finds that well moistened strontium hydroxide, kept for some time at 50° in an atmosphere of aqueous vapour having a tension of 16 mm., is converted into the dihydrate of strontium oxide. When exposed to a current of dry carbonic anhydride, the dihydrate is decomposed into the carbonate, but the product dried at 145° is deficient in carbonic anhydride and contains water. In opposition to Heyer's statement that carbonate alone is formed under these conditions, the author regards this fact as evidence that, in addition, a hydrated basic carbonate is also formed. The basic carbonate is a neutral compound which, in an atmosphere of carbonic anhydride, slowly absorbs that gas. It does not lose its water completely at 120°, but must be raised to incipient redness before complete dehydration occurs; no evolution of carbonic anhydride occurs at this temperature, but the product on moistening with water is strongly alkaline. W. P. W.

Estimation of Water in Strontia Dihydrate. By C. Heyer (*Ber.*, **19**, 3222—3224).—The author does not believe in the existence of a basic strontium carbonate, and ascribes the analytical results obtained by Finkener (preceding Abstract) to the use of too great an amount of substance (Finkener used over 5 grams), as not more than 0·5 gram should be used to ensure complete decomposition (compare this vol., p. 108). N. H. M.

Vapour-density of Zinc. By J. Mensching and V. Meyer (*Ber.*, **19**, 3295—3298).—In their paper, the authors describe the method used by them in the determination of the vapour-density of zinc, and give details of the furnace employed, with which a constant temperature of about 1400° was obtainable under the conditions of working. The porcelain experimental tube was filled with nitrogen carefully freed from every trace of oxygen by slow passage over red-hot copper turnings, and through chromous chloride and alkaline pyrogallate. Two experiments were made, one at a temperature lower than the maximum, the second at the maximum temperature of the furnace, and the numbers obtained for the density were 2·41 and 2·36 respectively, compared with 2·25, the theoretical density of monatomic (Zn) zinc vapour. Experiments were also made with magnesium, but so far without success, since it has not been found possible to volatilise the metal in hydrogen. W. P. W.

Ammonio-mercuric Chromates. By C. Hensgen (*Rec. Trav. Chim.*, **5**, 187—198).—On dissolving mercuric oxide in ammonium dichromate, Hirzel obtained a compound to which the formula $(NHg_2OH_2)_2,4HgCrO_4$, was ascribed, although based only on determinations of the mercury and chromium. In this paper, it is shown that mercuric oxide dissolves readily in a saturated solution of ammonium dichromate; golden, crystalline leaflets or needles separate out; these are insoluble in water, alcohol, and ether, very soluble in hydrochloric acid, but only sparingly soluble in dilute nitric or sulphuric acid. Analytical results showed the atomic ratio Hg : N : Cr = 1 : 2 : 2, and that three-fourths of the total nitrogen was in the form of ammonium and the remainder in an amido-group, results which point to the composition $(NHg_2,H_2O)_2,Cr_2O_7,3(NH_4)_2Cr_2O_7$. These crystals when treated with excess of ammonia yield a canary-yellow powder, which no longer contains nitrogen in the form of ammonium, and to which the formula $(NHg_2,H_2O)_2CrO_4$ is ascribed. If mercury chromate be digested with a warm, concentrated solution of ammonium dichromate, a brown solution is obtained, from which, on pouring into an excess of cold water, a yellow powder is deposited; the composition of the substance is $(NHg_2,H_2O)_2CrO_4$, the analogue of the selenate $(NHg_2,H_2O)_2SeO_4$. V. H. V.

Water of Crystallisation of Alums. By E. Maumené (*Compt. rend.*, **103**, 1140—1141).—Ordinary potassium-alum, containing according to the author 28·73 mols. H_2O, was dried for several months over sulphuric acid almost completely free from water. It never shows any condition of equilibrium corresponding with the formation of a hydrate containing 24 mols. H_2O. Towards the end of the operation, dehydration took place very slowly. The product contains 3·5 mols. H_2O, and seems to have attained a condition of equilibrium. C. H. B.

Chemical Composition of some Ancient Ceramics from Brandenburg. By E. Jensch (*Ber.*, **19**, 2850—2853).—Fragments of urns from various ancient burying places were analysed. The following may be quoted as examples:—I. From the urn field between

Reichersdorf and Küppen, Jessnitz N/L. II. Fünfeichen, Fürstenberg a/O. III. Platkow, Gusow, in the Lebus district.

The specimen II was taken from the sides, which were covered with a thin glaze, I and III were taken from the bottom of the urns. Specimen II was coarse-grained and porous. Dried at 105° the loss of weight varied between 0·6—5·3 mean 1·95 per cent., an additional loss of 1·5—9·4, mean 4·0,2 per cent., occurring when the temperature was raised to a red heat.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Alkalis.
I.	62·46	27·27	3·17	0·44	1·21	0·89	2·93
II.	61·32	36·57	1·07	0·33	0·18	0·24	0·13
III.	64·57	27·70	1·77	—	2·83	0·28	0·69

	P_2O_5.	SO_3.	MnO.	Total.
I.	0·01	0·11	0·23	98·73
II.	—	—	—	99·84
III.	0·75	—	0·27	98·66

Owing to the unusual amount of phosphoric acid, analyses of five other fragments from the two urns containing the highest amount were made, with a result that a variation of 0·26—0·85 per cent., and 0·12—0·97 per cent. respectively were found. This is in all probability accounted for by imperfect admixture of bone-ash or some material rich in phosphorus with the red clay of the district which was most probably used in the manufacture of the urns. The clay accompanying the urn from Linderode had the composition SiO_2, 62·67; Al_2O_3, 29·34; FeO and Fe_2O_3, 3·56; CaO, 1·17; MgO, 0·53; Alkalis, 2·02. W. P. W.

Heating and Cooling of Fused Steel. By Osmond (*Compt. rend.*, **103**, 1135—1137).—Iron containing 0·16 per cent. of carbon shows a feeble perturbation at 749° (this vol., p. 14), but the modification of the iron takes place mainly at a higher temperature. In the cooling of the fused metal, there are in fact three points at which the rate of cooling diminishes. Between 863 and 820°, the maximum effect being observed between 845° and 839°; between 775° and 736°, the maximum being between 763° and 749°; and between 693° and 669°. The first change indicates the return of the iron from the β modification which is stable at high temperatures, to the ordinary modification stable at the ordinary temperature, this return being retarded by the presence of the small quantity of carbon. The first diminution in the rate of cooling corresponds with a development of +3·8 cal. and the second with a development of +1·3 cal., the total 5·1 agreeing closely with Pionchon's determination +5·3 cal. On reheating, the second and third perturbations become coincident.

With steel containing 0·57 per cent. of carbon, the two perturbations at the highest temperatures become merged into one which takes place at 736—690°, but is still quite distinct from recalescence. If the steel contains 1·25 per cent. of carbon, the temperature at which alteration takes place is still lower, and in fact coincides with recalescence at

704°. It is evident that during cooling the presence of the dissolved carbon retards the alteration of the iron the more completely the greater its quantity.

Steel containing 0·16 per cent. of carbon shows the same perturbations in an atmosphere of hydrogen as in nitrogen. Steel containing 1·25 per cent. of carbon when cooled in hydrogen from 800° shows much enfeebled recalescence, a result probably due to the fact that hydrogen, as Forquignon has shown, has a strong attraction for the carbon in steel, and thus diminishes the proportion of carbon which combines with the iron. In another experiment, however, cooling from 1100°, no anomalies were observed.

No noteworthy differences are observed in an atmosphere of coal-gas.

C. H. B.

Influence of Silicon on the Condition of Carbon in Cast-iron. By F. Gautier (*Compt. rend.*, **103**, 1137—1140).—The author has repeated Stead and Wood's experiments in which white iron was converted into grey iron by melting with a certain proportion of iron rich in silicon. His results were precisely the same, and show that in presence of not less than 2 per cent. of silicon the combined carbon is almost completely changed into graphite. He points out that the reverse change takes place in the Bessemer process. About half the silicon is removed before the amount of carbon has appreciably diminished, and it is then found that the iron has become white. The presence of manganese interferes with the conversion of combined carbon into graphite, owing to the tendency of the manganese to combine with carbon.

Grey iron prepared indirectly in this way is more homogeneous and has greater tenacity than grey iron obtained in the ordinary way.

C. H. B.

A New Class of Cobaltic Salts. By F. Kehrmann (*Ber.*, **19**, 3101—3103).—*Potassium cobaltic oxalate*, $K_6Co_2(C_2O_4)_6 + 6H_2O$, is obtained by mixing cobaltic hydroxide, potassium oxalate, oxalic acid, and water to a thick paste, and allowing the mixture to remain 14 to 21 days. After recrystallisation, &c., the salt is obtained in nearly black, well-formed, seemingly monosymmetric crystals, which in thin lamellæ show distinct dichroism (dark blue and emerald-green).

When treated with cold saturated sodium chloride solution, the sodium potassium salt is obtained crystallising in beautiful pyramids. The barium salt crystallises in sparingly soluble, green needles. The solutions of these salts are stable in the cold, but quickly decompose on heating with evolution of carbonic anhydride and formation of cobaltous salts. Corresponding nickel compounds could not be obtained.

A. J. G

Mineralogical Chemistry.

Occurrence of Free Iodine in a Mineral Water. By J. A. Wanklyn (*Chem. News*, **54**, 300).—The water from Woodhall Spa, near Lincoln, is exceptionally rich in bromides and iodides, and, moreover, contains iodine in sufficient quantity to give it a brown tint. On agitating it with carbon bisulphide, the water is decolorised, the bisulphide becoming violet. D. A. L.

Gold from Burmah. By R. Romanis (*Chem. News*, **54**, 278—279).—The samples were found on the banks of the Meza, a tributary of the Irrawaddi, about 30 miles from the latter river, and to the westward of Katha. Sample A.—Large irregular fragments with quartz embedded in some of them. Iridosmine and crystals of chrome iron can be separated under a microscope. The composition is given below. The silver ore is a grey mineral which loses 49 per cent. on ignition. Sample B.—Fine smooth grains; about 17 per cent. insoluble in aqua regia, the insoluble matter consists of quartz, zircon, and about 7 per cent. of iridosmine in bright, flat grains mixed with a black mineral apparently a platinum ore.

A.

	Gold	87·66
	Silver	5·96
Gangue.	Copper pyrites	1·95
	Quartz	1·09
	Magnetic oxide of iron	0·32
	Silver (? ore)	1·54
	Loss on ignition	1·48

B.

Gold	74·83
Silver	2·86
Platinum	2·53
Iridosmine	7·04
Zirconia	7·08
Silica (by diff.)	5·66
Magnetic oxide of iron	a little

D. A. L.

Preparation of Crystallised Insoluble Carbonates. By L. Bourgeois (*Compt. rend.*, **103**, 1088—1091).—0·5 gram of the amorphous carbonate is heated in a tube at 150—180°, with 20 c.c. of water and 2 grams of ammonium chloride, and then very slowly cooled. After the process of heating followed by slow cooling has been repeated four or five times, the carbonate becomes completely crystallised. The ammonium chloride is partially converted into carbonate, which decomposes into ammonia and carbonic anhydride. Part of the insoluble carbonate is thus dissolved, and separates in crystals during the slow cooling. When the heating is repeated, the

same changes take place, and the crystals gradually increase at the expense of the amorphous substance. Calcite is obtained in simple rhombohedrons without admixture with aragonite; strontianite is obtained in short, rhombic prisms; witherite in long, thin, fibrous needles; cerusite in long, striated needles, which are always mixed with a variable proportion of a hydrated carbonate in nacreous, hexagonal lamellæ, with negative uniaxial double refraction, which is probably identical with hydrocerussite. Cadmium carbonate crystallises in rhombohedrons similar to those of calcite.

Lithium, magnesium, zinc, manganese, iron, nickel, cobalt, and copper carbonates yield only amorphous precipitates or indistinct spheroliths.

Almost identical results are obtained by heating the carbonates at 140° with a solution of urea, which is converted into ammonium carbonate by hydration. In addition, copper yields small prisms, which seem to be identical with malachite. C. H. B.

Occurrence of Iodine in Phosphorites and of Lithium in Psilomelane. By F. Sandberger (*Jahrb. f. Min.*, 1887, **1**, Mem., 95). — The author notes the remarkable manner in which elements occurring in rocks in very minute quantities become concentrated in certain products of the decomposition of the rocks. This is the case with iodine, which the author has detected in the staffelite from Brilon in Westphalia, separated out from decomposed diabase, and in the osteolite from the weathered basalts of the Kreuzberg on the Rhone.

Not less remarkable is the concentration of small quantities of lithium in psilomelane, a fact first observed in the Saxon Ore Mountains, but subsequently by the author in various places in the Black Forest. Lithium also becomes concentrated in the hexagonal variety of zinc sulphide, the so-called *schalenblende*. B. H. B.

Nephrite from Alaska. By A. B. Meyer (*Jahrb. f. Min.*, 1887, **1**, Ref., 6—8).—The author describes two axes procured from the Indians of South-east Alaska. The smaller has a sp. gr. of 2·96, and contains some magnetite; the sp. gr. of the larger being 2·92. The hardness of the latter is somewhat less than is usual with nephrite; the material being no longer quite unaltered. Analysis of the latter gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
51·63	4·31	4·82	10·45	22·36	4·84	98·41

Under the microscope, it was found that this nephrite resembles most closely that from the river Kitoj in East Siberia. It differs from this, however, in the absence of all accessory constituents, except magnetite.

Green nephrite has been found *in situ* at the extreme north-west of Alaska. The raw material brought from Point Barrow in Alaska by Baird, proves on analysis to be neither nephrite nor jadeite, but pectolite. B. H. B.

Prehnite from Silesia. By A. Beutell (*Jahrb. f. Min.*, 1887, **1**, Mem., 89—94).—1. *Prehnite from Striegau.*—Prehnite has recently been found in the granite of Striegau. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Loss on ignition.	Total.
43·29	25·58	trace	26·36	4·77	100·00

These results correspond with the formula $Si_3O_{12}Ca_2Al_2H_2$. The mineral usually occurs in the form of compact masses, isolated crystals being occasionally met with. Thin sections under the microscope present the optical anomalies observed by Des Cloizeaux and Mallard in the prehnites of Connecticut and Arendal.

2. *Prehnite from Jordansmühl.*—An analysis of prehnite from Jordansmühl has been published by B. Schubert (Abstr., 1883, 35). To this the author now adds the results of an exhaustive crystallographical and optical investigation. The axial ratio he finds to be $a : b : c = 0·8420 : 1 : 1·1272$. B. H. B.

Porphyry from Horka in Prussia. By V. Steger (*Jahrb. f. Min.*, 1887, **1**, Ref., 42). — The porphyry occurring at Horka in Prussian Upper Lausitz exhibits a grey to dirty yellow ground-mass, containing numerous reddish-brown, small crystals of orthoclase and white crystals of oligoclase. Quartz occurs but rarely. As accessory constituents, the rock contains hornblende and sillimanite. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	P_2O_5.	K_2O.
58·74	14·96	8·75	3·68	1·59	2·62	3·60

Na_2O.	Loss on ignition.	Total.
3·22	2·87	100·03

In chemical composition, the Horka porphyry resembles most closely that from Vetakollen and Tyveholmen, near Christiania. It differs from these, however, in its percentage of phosphoric anhydride. B. H. B.

Analyses of Persian Eruptive Rocks. By E. Drasche (*Jahrb. f. Min.*, 1887, **1**, Ref., 65—66).—No. 1. Augite andesite, from the Elburs, near Bumehin, containing plagioclase and augite in a reddish-brown ground-mass. No. 2. Olivine diabase from the same locality; pale brown augite forming small irregular patches between plagioclase needles. The olivine is for the most part altered. No. 3. Plagioclase basalt from Bumehin, exhibiting a porphyritic structure; augite, plagioclase, magnetite, and iron-glance, occurring in a colourless magma. The olivine originally present is entirely decomposed. No. 4. Black rock from Tschemerin Kuschkek, appearing under the microscope as a compact mass containing numerous granules, in which plagioclase, a chloritic mineral, and apatite have separated out.

	No. 1.	No. 2.	No. 3.	No. 4.
SiO_2	55·10	47·51	50·53	55·67
Fe_2O_3	8·52	16·26	11·76	10·89
Al_2O_3	19·57	16·00	18·36	16·06
CaO	5·90	7·63	9·33	5·92
MgO	2·01	7·38	4·40	2·93
K_2O	4·77	1·01	3·23	0·51
Na_2O	3·67	2·29	2·07	3·81
P_2O_5	—	—	—	0·83
Loss on ignition	1·19	3·25	1·35	4·15
Totals	100·73	101·33	101·03	100·77

B. H. B.

Investigations on Ore-veins. By F. Sandberger (*Jahrb. f. Min.*, 1887, **1**, Mem., 111—113).—To complete his investigations on ore-veins, the author has collected pure material in quantity sufficient to enable a dry silver assay to be made of the silicates. The substances employed did not contain a trace of intermixed sulphides. The mica from the gneiss of Schapbach was found to contain 0·001 per cent. of silver, and the augite from the granular diabase of St. Andreasberg in the Harz also contained 0·001 per cent. of silver. Nine years ago the author proved that lead, antimony, zinc, cobalt, copper, nickel, and arsenic were present in this augite. Consequently the elements of all the Andreasberg ores are shown to be present in it. B. H. B.

Recent Alluvial Deposits in the Ij and the Zuyder Zee. By J. M. Van Bemmelen (*Rec. Trav. Chim.*, **5**, 199—218).—In this paper, analyses are given of the recent deposits of eminently fertile clay in the Zuyder Zee and Ij, with especial reference to the proportion of chlorides, sulphates, magnesium and calcium carbonates, and phosphoric acid, together with the composition of the silicates. In some localities, there was a considerable accumulation of iron pyrites, especially on the small ancient islands, along the banks of lakes of brackish water, and in the soil in which plants have taken root and formed deposits of turf. The chemical changes which lead to this accumulation, consists in the simultaneous reduction of ferric oxide and sulphuric acid, accompanied by a slow disappearance of calcium carbonate. The ferrous sulphide thus formed is converted into pyrites as Bunsen has previously explained. Analyses of certain clays showed from 2 to 5 per cent. of pyrites. When these clays are dried and exposed to the action of the air, a contrary action takes place, the pyrites being reconverted into ferric sulphate, which is deposited in the form of a bright yellow, amorphous mould, this being ultimately converted by rain into a very basic insoluble sulphate. The paper is illustrated by numerous analytical results.

V. H. V.

Mineral Waters from Java. By S. Meunier (*Compt. rend.*, **103**, 1205—1207).—Three springs from Kapouran, near Boghor, in the kingdom of Kouripan, were examined. The waters were found to contain the following proportions of solid matter in grams per

litre:—Great Green Spring, 15·87; Hot Spring, 27·00; High Platform Spring, 28·78.

The relative proportions of the constituents are practically the same in all three springs:—

Calcium chloride	54·203
Magnesium chloride	40·651
Sodium chloride	2·860
Potassium chloride	1·104
Residue insoluble in water	1·924
	100·742

The portion of the residue insoluble in water consists of minute crystals of calcium magnesium carbonate, resembling those of dolomite.

These springs are characterised by the absence of carbonates and the presence of a large proportion of calcium chloride. They belong to a hydrological group, representatives of which are found in the Cauquenès, Chili; Tinguiririca, Peru; Savu Savu, in the Fiji Islands; Berg Giefshubel, Saxony; and Pitkeathly, Scotland.

C. H. B.

Organic Chemistry.

Russian Petroleum. By J. A. Le Bel (*Compt. rend.*, **103**, 1017—1019).—It is well known that American petroleum consists mainly of paraffins, whilst Bakû petroleum consists mainly of naphthenes, C_nH_{2n}, and naphthylenes, C_nH_{2n-2}. Boussingault has shown that Alsatian petroleum contains other hydrocarbons.

At Tiflis, a petroleum is obtained with a composition similar to that of the American oil, and in the Crimea heavy and light petroleums are obtained from neighbouring strata. The following table gives the sp. gr. of corresponding fractions of oil from different sources:—

		Sp. gr.
Pennsylvania	236—240°	0·81
Bakû	240—241	0·83
Alsace	235—245	0·86
Tschungnelek (Crimea)	235—245	0·89

The Crimean oil contains 87·4 per cent. of carbon and 12·5 per cent. of hydrogen. The differences in sp. gr. are greater than the differences in the amount of carbon, and these differences do not remain constant when the more volatile fractions are examined:—

		Sp. gr.
Pennsylvania	92—94°	0·690
Bakû	90—95	0·738
Bakû	90—91	0·747
Tschungnelek.....	80—93	0·750
Toluene hydride	96—97	0·758

The more volatile fractions of the Crimean oil are very similar to the corresponding fractions of the oil from Bakû, and differences only become evident with the fractions boiling above 150°. The sp. gr. of the Russian oils agrees with that of toluene hydride, with which Beilstein and Kurbatow regard them as identical. It may also be supposed that the Russian oil contains naphthenes belonging to the trimethylene series; in this case it should contain a term C_6H_{10}, boiling at 30—35°, with a sp. gr. about 0·04 higher than that of the corresponding fraction of American oil. If, on the other hand, these naphthenes are hydrides of the benzene series, the first term would be C_6H_{12}, boiling at 70°.

It is found that fractions of Bakû oil boiling at 30—35° have a sp. gr. which agrees closely with that of the same fraction of American oil, and also with that of pentane boiling at 30°. The differences only become evident with the fractions above 60°, and it may be taken that the Russian oils boiling above 60° contain no naphthenes, a result which confirms Beilstein and Kurbatow's conclusion as to their identity with the benzene hydrides.

C. H. B.

Action of Heat on Ethylene. By L. M. Norton and A. A. Noyes (*Amer. Chem. J.*, **8**, 362—364; compare Abstr., 1886, 604 and 781).—Ethylene was slowly passed through a hard glass tube heated to dull redness, the escaping gases passed through condensing tubes, ammoniacal cuprous chloride and bromine, samples of the gases being ultimately collected. After a month, 15 c.c. of liquid had been condensed, and was found to contain benzene, naphthalene, and anthracene; only a very slight precipitate was formed in the cuprous solution. There were about 300 grams of bromides of unsaturated hydrocarbons, consisting largely of ethylene bromide; but methylene, propylene, and butylene bromides were also present, as well as a solid bromide.

The solid bromide is identical in composition and properties with the crotonylene tetrabromide obtained from coal-gas, from crotonylene from erythrol and from oil-gas, it is, therefore, divinyl, $CH_2:CH\cdot CH:CH_2$. The escaping gases consisted of methane and ethane. The author believes that the aromatic hydrocarbons are formed directly from the ethylene without the intermediate formation of acetylene. H. B.

Reaction of Organic Bisulphides and Bisulphoxides with Potassium Sulphide. By R. Otto and A. Rössing (*Ber.*, **19**, 3129—3132).—When the bisulphides of ethyl, amyl, phenyl, paratolyl, or benzyl are treated with potassium sulphide in alcoholic solution, they are converted into the corresponding mercaptides according to the

equation $X_2S_2 + 2K_2S = 2XSK + K_2S_2$, the reaction thus seeming to be general for organic sulphides.

Potassium bisulphide seems to be without action on these bisulphides.

In like manner the thiosulphonates of the general formula $RSO_2{\cdot}SR$ are decomposed by potassium sulphide into the potassium salts of the thiosulphonic acids and potassium mercaptides.

In a foot-note, the following boiling points are given:—Paratoluene hydrosulphide 190·2—191·7°. Paratoluene bisulphide begins to boil at 307° (thermometer in liquid), but is in great part decomposed during the distillation. Phenyl bisulphide begins to boil at 320°, but is also in great part decomposed on distillation.

A. J. G.

Action of Alcohols on Aurophosphorous Chloride. By L. Lindet (*Compt. rend.*, **103**, 1014—1017).—*Triethyl chloraurophosphite*, $Et_3PAuClO_3$, is obtained by allowing absolute alcohol to drop on a mixture of dry aurous chloride and phosphorus, both of which are immediately dissolved. The product is mixed with water, and the insoluble, oily ethereal salt is separated. Ethyl phosphite dissolves aurous chloride, and yields an oil identical in appearance with triethyl chloraurophosphite, but the product could not be purified. The ethereal salt is also obtained by dissolving aurous chloride in a solution of ethyl phosphite in alcohol, prepared by Railton's method of allowing phosphorus trichloride to drop into a large excess of absolute alcohol.

Triethyl chloraurophosphite is a liquid which solidifies to a white, crystalline mass at about −10°. It is not volatile, and is stable when exposed to air at the ordinary temperature, but begins to decompose at 100°; sp. gr. = 2·025. It is insoluble in water, but dissolves in alcohol, ether and benzene. Ammonia dissolves it readily, with formation of the compound $Et_3PAuClO_3 + 2NH_3$, which is obtained in somewhat deliquescent leaflets by evaporating the ammoniacal solution at 40°. This compound dissolves in water, and when the solution is acidified the ethereal salt is precipitated. Triethyl chloraurophosphite also dissolves in potassium hydroxide solution, and is reprecipitated on adding an acid. If the solution is concentrated on the water-bath, or in a vacuum at the ordinary temperature, the ethereal salt separates as an oil mixed with crystals of potassium hydroxide, but both dissolve on addition of water. At 100°, potassium chloride and potassium aurite are formed, but the ethereal salt is not completely decomposed unless evaporated to complete dryness in presence of excess of potassium hydroxide. Under these conditions, gold separates in the metallic state.

Propyl, butyl, and amyl alcohols yield similar products.

Trimethyl chloraurophosphite, $Me_3PAuClO_3$, is obtained by the action of pure methyl alcohol on aurous chloride and phosphorus. It forms slender, colourless needles, which melt at 100—101°, alter slightly when exposed to air, and do not volatilise without decomposition. It is insoluble in water, and is somewhat less soluble than the ethyl-compound in alcohol, ether and benzene. It also dissolves in methyl alcohol.

C. H. B.

Dextrorotatory Hexyl Alcohol from Essence of Chamomile. By P. v. Romburgh (*Rec. Trav. Chim.*, **5**, 219—227).—By frequent fractional distillation of essence of Roman chamomile, a dextrorotatory alcohol (*methethopropyl alcohol*), $CHMeEt{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained, boiling at 154°; sp. gr. 0·829 at 15°; $[\alpha]_D = 8{\cdot}2$ at 17°. On oxidation with chromic mixture, the alcohol yields a dextrorotatory caproic acid (*methethopropionic acid*), $CHMeEt{\cdot}CH_2{\cdot}COOH$, boiling at 196—198°; sp. gr 0·930 at 15°; $[\alpha]_D = 8{\cdot}92$. Its calcium and silver salts crystallise in needles, and its amide in long needles melting at 124°, soluble in water. A hexyl caproate is formed as a subsidiary product of oxidation. This boils at 233—234° with slight decomposition; sp. gr. 0·867 at 15°; $[\alpha]_D = 12{\cdot}86$ at 19°. As both the alcohol, and also the acid obtained therefrom, are optically active substances, according to the hypothesis of Van't Hoff and Le Bel they must contain an asymmetrical carbon-atom. Of the three possible hexyl alcohols satisfying this condition, two have been identified by Lieben and by Zeisel and Silva. The alcohol now described must therefore have the remaining formula, that ascribed to it above. V. H. V.

Thiodiglycol-compounds. By V. Meyer (*Ber.*, **19**, 3259—3266).—Thiodiglycol is obtained by treating a concentrated aqueous solution of potassium sulphide with glycol chlorhydrin. The product is evaporated on a water-bath and extracted with alcohol. It is a syrup almost without odour.

Thiodiglycol chloride, $S(CH_2{\cdot}CH_2Cl)_2$, is formed by gradually mixing phosphorus chloride with thiodiglycol (kept cool), and pouring the product into water. It is an oil having a slight, sweet, ethereal odour. When cooled in ice-water, it solidifies to long prisms. It boils at 217°, and is almost insoluble in water. It has very poisonous properties: a rabbit exposed to air previously passed over filter-paper saturated with the substance died in three days.

When ethylene bromide is heated to boiling for a long time with aqueous potassium sulphide, an amorphous, insoluble product is obtained, differing from the polymerised diethylene disulphide (formed by adding ethylene bromide gradually to a solution of potassium sulphide in alcohol). It remains unchanged when boiled for days with phenol. The polymeride, which is decomposed by boiling with phenol, can also be prepared by adding ethylene bromide to the sodium salt, $C_2H_4(SNa)_2$, covered with a little alcohol; if 50 times the weight of alcohol is used, the whole well cooled, and the bromide gradually added, diethylene disulphide is obtained.

The author is making experiments with a view to synthesise the ethyl vinyl ether of thioglycol, $SEt{\cdot}C_2H_4{\cdot}S{\cdot}CH : CH_2$, in order to compare it with the product obtained by the reduction of diethylene disulphide ethyl iodide (Mansfeld, this vol., p. 122). N. H. M.

Preparation of Derivatives of Carbohydrates. By E. Baumann (*Ber.*, **19**, 3218—3222).—*Tetrabenzoyl dextrose*, $C_6H_8O_6Bz_4$, is prepared by mixing a solution of 5 grams of grape-sugar in 15 c.c. of water with 210 c.c. of a 10 per cent. soda solution, adding 30 c.c. of benzoic chloride, and shaking until the odour of the chloride disappears. It

is insoluble in water, readily soluble in ether, alcohol, and benzene; it melts at 60—64°. It is only slowly decomposed by boiling acids or alkalis. 0·001 or 0·002 gram of grape-sugar dissolved in 100 c.c. of water can be detected by shaking with 2 c.c. of benzoic chloride and the corresponding amount of soda solution; the benzoyl-derivative separates as a flaky precipitate.

Hexabenzoyl saccharose, $C_{12}H_{16}O_{11}Bz_6$, is obtained in a manner similar to the above compound.

Tetrabenzoyl glucosamine, $C_6H_9NO_5Bz_4$, is prepared by shaking a solution of 5 grams of glucosamine in 20 c.c. of water with 140 c.c. of 10 per cent. soda solution and 20 c.c. of benzoic chloride. It is readily soluble in chloroform, insoluble in water, sparingly soluble in alcohol, from which it separates in long needles melting at 197—198°. It is completely decomposed by boiling with alkali.

Glycerol dibenzoate, $C_3H_5O_2Bz_2OH$, crystallises from light petroleum in long, colourless needles melting at 70°; it is very readily soluble in alcohol, ether, and chloroform, insoluble in water. N. H. M.

Formation and Composition of Humous Substances. By M. Conrad and M. Guthzeit (*Ber.*, **19**, 2844—2850).—In their previous papers (Abstr., 1885, 745; 1886, 138; this vol., p. 25), the authors have shown that when cane-sugar is inverted by dilute acids, the lævulose is more quickly and completely decomposed, and yields more humous substances than the dextrose. Ulmin is the chief product from lævulose, whilst from dextrose ulmic acid entirely soluble in aqueous potash is obtained. If a more concentrated acid is employed, the humous substances from dextrose are less soluble, and concentrated hydrochloric acid yields a product practically insoluble in cold aqueous potash. The authors draw the following conclusions from their experiments:—

(1.) That when saccharoses and glucoses are decomposed by dilute acids, the yield of humous substances stands in no direct relation to that of formic and acetopropionic acids. (2.) Saccharoses by the action of dilute acids first suffer hydrolysis, and the resulting glucoses, by the elimination of the elements of water, yield on the one hand formic and acetopropionic acids, and on the other humous substances. (3.) Saccharoses and glucoses, with the exception of lævulose, yield more humous substances by boiling with dilute (7—10 per cent.) hydrochloric acid than with sulphuric acid. (4.) The more concentrated the acid, the greater is the yield of humous substances. (5.) With dilute acids, lævulose yields more humous substances than dextrose. (6.) The percentage composition of the humous substances varies between 62·3—66·5 C and 3·7—4·6 H; those obtained by the action of concentrated acids containing the highest percentage of carbon.

The authors have confirmed Sestini's observation that air-dried humous substances when heated above 110° give off a vapour of acid reaction, and capable of reducing silver from solutions of its salts. W. P. W.

Arabinose. By H. Kiliani (*Ber.*, **19**, 3029—3036).—Arabinose is prepared by heating cherry gum (1 part) with 8 litres of 2 per cent. sulphuric acid for 18 hours in a water-bath, neutralising with hot,

saturated, aqueous baryta, and evaporating the solution (without filtering) to a small bulk; it is then shaken with much 96 per cent. alcohol. The clear solution is decanted, most of the alcohol distilled off, and the residue evaporated down; it is again shaken with alcohol, and the solution concentrated by distillation. On cooling, crystals separate; these are washed with alcohol and recrystallised from six or seven times their weight of alcohol (sp. gr. 0·825); the product is then pure.

Arabonic acid (Bauer, Abstr., 1885, 501) is prepared by shaking a solution of 20 grams of the sugar in 100 c.c. of water with 40 grams of bromine for an hour; the bromine is then removed by warming and the hydrobromic acid by means of silver oxide. Analytical results show that it is a tetrahydroxyvaleric acid, $C_5H_{10}O_6$, and not an acid of the formula $C_6H_{12}O_7$ (Bauer, *loc. cit.*). The calcium salt, $(C_5H_9O_6)_2Ca + 5H_2O$, and the barium salt which forms microscopic plates were analysed. The acid could only be obtained as a syrup.

Arabinosecarboxylamide, $C_7H_{15}O_7N$, separates as a fine, white, crystalline powder, when a clear solution of arabinose (1 part) in water (1 part) is mixed with 60 to 70 per cent. hydrocyanic acid, and kept for eight days in a closed vessel. It dissolves readily in water, but is insoluble in strong alcohol and ether; when heated, it becomes yellow at 130°, and decomposes completely at 160°, with evolution of gas. Boiling water and hot alkali solutions decompose it with evolution of ammonia.

The *lactone* of *arabinosecarboxylic* acid, $C_7H_{12}O_7$, is prepared by dissolving the amide in the corresponding amount of hot baryta-water, evaporating until the odour of ammonia has disappeared, and precipitating the barium exactly with sulphuric acid. The filtrate is made clear by the addition of a few drops of hydrochloric acid, and evaporated. It crystallises from water in very lustrous prisms (probably rhombic), melting at 145—150°; it is very sparingly soluble in alcohol. It has nearly the same rotatory power as the lactone of dextrosecarboxylic acid; $[\alpha]_D = -54{\cdot}8$. The *calcium* and *barium salts* are amorphous.

The mother-liquor from the preparation of arabinosecarboxylamide contained chiefly ammonium arabinosecarboxylate. N. H. M.

Decomposition by Heat of the Nitrates of the Paraffinoïd Amines. By P. v. Romburgh (*Rec. Trav. Chem.*, **5**, 246—251).—The decomposition of ammonium nitrate may be explained on the supposition that the nitrite is at first formed, on which the oxygen liberated acts to form an unstable combination, $NH_2OH,NO{\cdot}OH$, which in its turn is decomposed into water and nitrous oxide. If this were the interpretation of the reaction, the nitrates of the paraffinoïd amines should yield a nitrosamine as a product of their decomposition, thus: $NMe_2H,OH{\cdot}NO_2 = NMe_2H,OH{\cdot}NO + O = NMe_2{\cdot}NO + H_2O + O$; the liberated oxygen would partly oxidise either the salt or the nitrosamine formed.

Dimethylamine nitrate decomposes at 150°, with evolution of nitrogen and carbonic anydride; and from the residue dimethylnitrosamine is obtained, the yield of which is 50—54 per cent. of that

required by the above theory. Similarly also diethylamine nitrate is decomposed when heated at 170°, and the reaction becomes violent with rise of temperature; carbonic anhydride and nitrogen together with an inflammable gas are evolved, and from the residue diethylnitrosamine may be obtained.

Experiments on the decomposition of methylamine, ethylamine, and tetrethylammonium nitrate were not so successful.

V. H. V.

Action of Hydrogen Chloride on Mixtures of Aldehyde with Alcohols and Phenols respectively. By A. Claus and E. Trainer (*Ber.*, **19**, 3004—3011).—When a mixture of aldehyde and methyl alcohol (1 vol. : 2 vols.) is treated with hydrogen chloride at a temperature below 0°, dried, and treated with sodium isobutoxide, the chief product is dimethylacetal; methylisobutylacetal (from chlor-ether contained in the original product) is also formed; it boils at 124—128°. When equal mols. of aldehyde and methyl alcohol are used, dimethylacetal, methyl-isobutylacetal, and di-isobutylacetal are obtained; the last compound would be formed from α-dichloro-ether in the original product.

Ethyl alcohol and aldehyde give a good yield of α-chlor-ether together with diethylacetal and α-dichlor-ether (compare Wurtz and Frapolli, *Annalen*, **108**, 226).

Isoamyl alcohol and aldehyde (equal mols.) yielded *α-chlorethyl isoamyl ether;* when 2 mols. of the alcohol are used, *di-isoamylacetal*, $C_2H_4O_2(C_5H_{11})_2$, alone is formed. It boils at 209—211° (uncorr.). Isobutyl alcohol (1 mol.) gave a better yield of monochlorether than amyl alcohol, and in the reaction with 2 mols. of alcohol a small amount of α-chlorethylisobutylacetal (boiling at 155—160°) could be isolated.

Ethylidene diphenyl, $CHMe(C_6H_4{\cdot}OH)_2$, is obtained by passing hydrogen chloride through a mixture of aldehyde (1 mol.) with phenol (2 mols.). It is readily soluble in alcohol, ether, chloroform, &c., insoluble in water, benzene, and light petroleum; it could not be obtained in the crystalline state. It softens at 100°, and becomes viscous at 125°. Aqueous alkali dissolves it readily.

Ethylidene-di-α-naphthol is formed in a similar manner, and is completely analogous in its properties to the diphenyl-derivative.

When β-naphthol and aldehyde are treated with hydrogen chloride, a crystalline *compound*, melting at 162—163°, is formed, having the formula $C_2H_4O_2(C_{10}H_7)_2$. It has none of the properties of a phenol, but corresponds with the acetals. The authors consider that this different behaviour of α- and β-naphthol (the one behaving like a phenol and the other like a fatty alcohol) is fresh evidence in favour of his unsymmetrical naphthalene formula. N. H. M.

Acid Propionates and Butyrates. By W. G. Mixter (*Amer. Chem. J.*, **8**, 343—346).—The following salts are described: *Acid barium propionate*, $(C_3H_5O_2)Ba,C_3H_6O_2 + 3H_2O$, forms tabular crystals that very slowly lose water and acid in dry air. *Acid strontium propionate*, $(C_3H_5O_2)_2Sr,C_3H_6O_2 + 3\frac{1}{2}H_2O$, forms long, thin

crystals, that lose acid on exposure to the air. *Acid calcium propionate*, $2(C_3H_5O_2)_2Ca,C_3H_6O_2 + 5H_2O$, forms long needles, that have an acid reaction and decompose on heating. *Acid barium isobutyrate*, $(C_4H_7O_2)_2Ba,C_4H_8O_2$, was obtained by heating a solution of the normal salt with the excess of the acid at 100° until constant.

H. B.

Preparation of β-Iodopropionic Acid. By V. Meyer (*Ber.*, **19**, 3294—3295).—The author finds that β-iodopropionic acid can be readily prepared from the glyceric acid obtained by the oxidation of glycerol with nitric acid, since the accompanying products neither form crystalline compounds with phosphorus iodide, nor interfere with the crystallisation of the iodo-acid. The syrup obtained by the oxidation of glycerol and subsequent removal of nitric acid, is diluted with water to a sp. gr. of 1·26, and 30 c.c. of the solution is then poured into a flask containing phosphorus iodide prepared from 50 grams of iodine and 6·5 grams of yellow phosphorus. A vigorous action takes place either in the cold or on gently warming, and the contents of the flask on cooling solidify owing to the separation of β-iodopropionic acid in large, colourless laminæ, which after one crystallisation from water are quite pure. W. P. W.

Methylisopropylacetic Acid. By P. v. Romburgh (*Rec. Trav. Chem.*, **5**, 228—239).—Köbig concluded that the caproic acid obtained by the oxidation of the hexyl alcohol from the essence of Roman chamomile was identical with that obtained by Markownikoff from the nitrile derived from methyl isopropyl carbinol. This view is not confirmed in the present paper, in which it is shown that methylisopropylacetic acid is not identical with the caproic acid obtained from the essence of chamomile. Two methods were used for the synthetical formation of methylisopropylacetic acid, $CHMePr^{\beta}COOH$, namely, the conversion of ethyl sodiomalonate into the isopropyl-derivative, and this into the ethereal salt of methylisopropylmalonic acid, from which the acid itself was obtained by hydrolysis; this, when heated, readily decomposed into carbonic anhydride, and the corresponding acetic acid; (ii) the conversion of ethyl acetoacetate into ethylic methylisopropylacetoacetate and the decomposition of this by alkalis into methylisopropyl acetone and methylisopropylacetic acid. Of these methods, the former is preferable.

The acid boils at 189—191°; sp. gr. = 0·928 at 15°; its silver salt crystallises in delicate needles, and its amide in micaceous scales.

Methylisopropylacetone, $CHMePr^{\beta}COMe$, boils at 135—140°, has a strong odour resembling menthol; sp. gr. = 0·815 at 20°; it does not seem to react with sodium hydrogen sulphite or with phenyl hydrazine.

Methylisopropylmalonic acid, $CHMePr(COOH)_2$, is crystalline, melts, though not very definitely, at 124°; its silver and calcium salts are sparingly soluble; its ethyl salt is a colourless liquid boiling at 221°; sp. gr. = 0·990 at 15°; it has an agreeable odour. As a subsidiary product, isopropylmalonic acid was obtained, a substance previously described by Conrad and Bischoff. V. H. V.

Derivatives of Erucic and Brassic Acids. By C. L. Reimer and W. Will (*Ber.*, **19**, 3320—3327).—Erucic acid is best obtained by saponifying rape oil with alcoholic potash, distilling off the alcohol, and dissolving the acid liberated on addition of sulphuric acid in three times its volume of 95 per cent. alcohol; on cooling to 0° crystals of erucic acid separate in an almost pure condition. The melting point of the acid was found to be 34°. *Ethyl erucate*, $C_{22}H_{41}O_2Et$, is a colourless, odourless oil, boiling above 360° without decomposition; its vapour-density, however, could not be determined. The *anhydride*, $C_{44}H_{82}O_3$, is prepared by heating erucic acid and phosphorus trichloride in molecular proportions. It is an oil crystallising in a freezing mixture to a mass of scales, and is very readily soluble in ether, benzene, and chloroform, sparingly soluble in alcohol. The *amide*, $C_{22}H_{41}O(NH_2)$, crystallises in colourless needles, melts at 84°, and is readily soluble in ether and benzene, sparingly soluble in alcohol, insoluble in water. The *anilide* is crystalline, melts at 55°, and is readily soluble in ether and benzene, sparingly soluble in alcohol.

Dierucin, $C_3H_5OH(C_{22}H_{41}O_2)_2$.—When rape oil is allowed to stand for a long time, a yellowish, tallow-like deposit is frequently found in the casks; this by repeated solution in ether and subsequent addition of alcohol can be obtained in silky needles. Dierucin melts at 47°, and is readily soluble in ether and light petroleum, insoluble in cold but soluble in hot alcohol. A trierucin could not be separated from rape oil.

Brassic acid is best prepared by warming erucic acid with dilute nitric acid to the melting point and then adding sodium nitrite; the product is quite pure after two crystallisations from alcohol. The *ethyl* salt is obtained directly from the acid, or by the action of nitrous acid on ethyl erucate; it crystallises in laminæ showing a vitreous lustre, melts at 29—30°, and boils above 360° without decomposition; the vapour-density could not, however, be determined. The *anhydride*, $C_{44}H_{82}O_3$, formed by heating the acid with phosphorus trichloride, crystallises in lustrous tables, melts at 28—29°, and is insoluble in water and alcohol, readily soluble in ether and benzene. The *amide* melts at 90°, and resembles in its properties the amide of erucic acid; both amides can be obtained by heating the corresponding ethyl salts to 230° with ammonia.

Tribrassidin is formed when rape oil (100 parts) is treated with nitric acid of sp. gr. = 1·2 (5 parts) and sodium nitrite (1 part); after some time, the resulting crystalline mass is washed, dissolved in ether, and from the solution cooled to 0° a lustreless, crystalline powder is obtained. Tribrassidin melts at 47°, but when heated above its melting point and allowed to cool, the melting point is subsequently found to be 36°; it is insoluble in alcohol, readily soluble in ether and chloroform. *Dibrassidin*, $C_3H_5OH(C_{22}H_{41}O_2)_2$, is formed when dierucin is treated with nitrous acid; it forms feebly lustrous crystals, melts at 65°, and is less soluble in ether than tribrassidin.

By distilling the calcium salts of erucic and brassic acids, two ketones are obtained which seem to be different; they are both very sparingly soluble in alcohol. W. P. W.

Dry Distillation of Calcium Tetramethylenecarboxylate with Lime. By H. G. Colman and W. H. Perkin, Jun. (*Ber.*, **19**, 3110—3115).—The products of this reaction are much ethylene (together with hydrogen and small quantities of carbonic anhydride and methane), ditetramethylene ketone, and an oil boiling at 136—137°, and uniting with hydrogen sodium sulphite, phenylhydrazine, and hydroxylamine; this is either tetramethylenealdehyde or acetyltetramethylene, but there is not sufficient evidence to say which.

Ditetramethylene ketone, $CO(C_4H_7)_2$, is a colourless oil, of peppermint-like odour; it boils at 204—205°, gives a colourless, crystalline compound with hydrogen sodium sulphite, and is acted on by bromine with evolution of hydrogen bromide. The phenylhydrazine compound is obtained as a yellow oily precipitate. The *oxime*, $C_{19}H_{15}NO$, forms a colourless syrup. A. J. G.

Oxalimide. By H. Ost and A. Mente (*Ber.*, **19**, 3228—3230).—Oxamic acid is best prepared by heating hydrogen ammonium oxalate at 140°, stirring all the time, extracting with aqueous ammonia, and converting into the sparingly soluble barium salt. This is converted into the ammonium salt, and precipitated with hydrochloric acid. The yield is 16 per cent.

Oxalimide, $<^{CO}_{CO}>NH$, is obtained by treating 20 grams of oxamic acid with 50 grams of phosphorus pentachloride and 20 grams of phosphorus oxychloride, and heating at 80—90°. The product is put into ice-water, warmed at 40°, filtered, and extracted with water at 60°. It is purified by dissolving in very dilute, warm aqueous ammonia, precipitating with hydrochloric acid, and recrystallising from water. It forms very lustrous prisms, which seem to be monoclinic. It is sparingly soluble in water, more soluble in warm aqueous ammonia. Boiling water decomposes it into oxamide and oxalic acid. Concentrated aqueous ammonia converts it into oxamide. When a cold saturated solution of oxalimide is treated with mercurous chloride, a crystalline mercury salt, $C_2O_2N{\cdot}HgCl$, separates.

Oxalimide is also formed by the action of nitrous acid on comenamic acid (dihydroxypyridinecarboxylic acid). This reaction, together with the results of experiments made by v. Pechman and others, is in favour of the view that meconic and cumalinic acids are derivatives of pyridone, $C_5H_4O{\cdot}NH$. N. H. M.

Ethyl Oxalacetate. By W. Wislicenus (*Ber.*, **19**, 3225—3228). —*Ethyl oxalacetate*, $COOEt{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, is prepared by dissolving 20 grams of ethyl oxalate in 100 grams of absolute ether, adding 3 grams of sodium wire, and then gradually adding 12 grams of pure ethyl acetate. After 12 hours, the product is solid, and is then washed with absolute ether, and dried over sulphuric acid. The *sodium-derivative*, $C_8H_{11}O_5Na$, crystallises from absolute alcohol in microscopic, matted needles; it is decomposed by dilute sulphuric acid. The ethyl salt is a rather viscous oil, almost without colour and odour; it decomposes when heated. The dilute alcoholic solution

gives with ferric chloride an intense dark red coloration. When boiled with dilute alkali or baryta-water, it yields oxalic and acetic acids. Warm 10 per cent. sulphuric acid decomposes it with evolution of carbonic anhydride and formation of pyruvic acid. When saponified by Ceresole's method for the preparation of acetoacetic acid, *monethyl oxalacetate*, $C_6H_8O_5$, is obtained. The latter crystallises from benzene in stellate groups of needles, melting at about 90°. It is readily soluble in alcohol, ether, and water, and has a strongly acid reaction.

Phenylhydrazine ethyl oxalacetate crystallises in plates; when boiled with water, it yields an *acid*, $C_{10}H_8N_2O_3$ (analogous to that obtained by Knorr from phenylhydrazine ethyl acetoacetate (Abstr., 1884, 1377). This dissolves readily in alcohol, sparingly in water, and decomposes at about 250° without melting. N. H. M.

Glycuronic Acid. By H. Thierfelder (*Ber.*, **19**, 3148).—Bromine converts glycuronic acid into saccharic acid, thus showing the presence in the former acid of an aldehydic group, and also its close relation to dextrose. L. T. T.

Fermentation of Citric Acid. By F. Watts (*J. Soc. Chem. Ind.*, **5**, 215—218).—Warington (this Journal, 1875, 936) has made an attempt to ascertain the amount and nature of the volatile acids in concentrated Sicilian lemon-juice, with a view to determine the acids other than citric which occur in concentrated juice. When perfectly fresh juice is distilled, the distillate is neutral, and consists only of water, with a small amount of essential oil derived from the peel. It is thus clear that volatile acids are not normal constituents of the juice. When lemon-juice is allowed to remain for some days in an open vessel, a film of mould gradually forms on the surface, consisting of a large number of minute cells of *saccharomyces mycoderma*. If this juice is now distilled, the distillate is found to be acid. From an examination of the distillate purified by redistillation, the author infers the presence of acetic acid, traces of formic acid, and possibly some propionic acid, and indirectly the existence of ethyl alcohol, with possibly some propyl alcohol, and minute quantities of methyl alcohol in the original juice after fermentation. It is also shown by experiment, that under the influence of *saccharomyces mycoderma* citric acid is split up directly into carbonic anhydride and water, oxygen being absorbed. It was found that the growth of this fungus ceased shortly after air was excluded. D. B.

Decomposition of Amides by Water and Dilute Acids. By Berthelot and André (*Compt. rend.*, **103**, 1051—1057).—Urea is decomposed by hydrochloric acid at the ordinary temperature. 100 c.c. of solution containing 1·0293 gram of urea was mixed with 10 c.c. of hydrochloric acid containing 3·78 grams of HCl, allowed to remain 24 hours, diluted with water, neutralised with magnesia, and the ammonia estimated by Schloesing's method. After boiling for one and a half hours about one-ninth of the total nitrogen in the urea was obtained in the form of ammonia (0·0523 gram). A similar

quantity of urea solution was boiled for an hour and a half with 2 grams of magnesia, and 0·0353 gram of ammonia was obtained, the amount evolved being practically the same in each half hour. The difference between the two quantities represents the ammonia formed by the action of hydrochloric acid in the cold, and is equivalent to the conversion of about 4 per cent. of the total nitrogen into ammonia in 24 hours. The action of the acid increases with the concentration, and also with the temperature.

It is well known that urea is partially decomposed when boiled with water. At the ordinary temperature, however, there is no appreciable decomposition, even after five days. Dilute sodium hydroxide solution decomposes urea slowly in the cold, but the action is much less marked than that of hydrochloric acid.

Asparagine is also decomposed by hydrochloric acid in the cold to a somewhat less extent than urea, and the decomposition increases with the concentration of the acid. It is decomposed by magnesia, as Boussingault observed, and also by boiling water, although only to a very slight extent. The action of soda is much more marked than with urea. 0·5 gram of asparagine mixed with 50 c.c. of water and 6 grams of sodium hydroxide, loses one-third of the total nitrogen in 24 hours, and about half of the total nitrogen in five days, or almost the whole of the nitrogen which is evolved as ammonia in the ordinary reaction.

Oxamide, when triturated with hydrochloric acid of 10 per cent., loses 0·7 per cent. of the total nitrogen in the form of ammonia in two hours. When boiled with magnesia, 6·3 per cent. of the total nitrogen is evolved as ammonia in the first half hour, and 3·4 per cent. in the second half hour. The first loss is due to the decomposition of the oxamide, and the second to decomposition of magnesium oxamate.

In all these cases the action of acids varies with the nature of the amide, is proportional to the time of action, and increases with the concentration of the acid and with the temperature.

The action of acids or alkalis on the amides derived from the alcoholic amines and from the hydroxy-acids will be different, since these amines are reconverted into ammonia with great difficulty. Hydrochloric acid tends to regenerate the amines from their derivatives, in consequence of the alkalinity of the amines. In the case of substances of complex function, like glycollamine and the leucines, both acids and alkalis will tend to produce the same azotised and oxygenised derivative, because each can combine with it.

Aspartic acid is not sensibly affected either by boiling water or by magnesia. Uric acid yields no ammonia when boiled with magnesia for an hour, but if triturated for two hours with hydrochloric acid of 10 per cent., it loses about 1 per cent. of the nitrogen in the form of ammonia. C. H. B.

Derivatives of Acetothiënone. By H. Brunswig (*Ber.*, **19**, 2890—2896).—*Bromacetothiënone*, $C_4SH_3{\cdot}CO{\cdot}CH_2Br$, prepared by the bromination of acetothiënone dissolved in carbon bisulphide, is a pale yellow oil, the vapour of which affects the mucous membrane. It cannot be distilled under ordinary pressures without decomposition;

at a low temperature it forms small, yellow crystals. The *anilide*, $C_4SH_3{\cdot}CO{\cdot}CH_2{\cdot}NHPh$, crystallises in leaflets melting at 80°; its acetyl derivative, $C_4SH_3{\cdot}CO{\cdot}CH_2{\cdot}NPhAc$, forms hard, brown crystals melting at 141·5°, and its nitroso-derivative, rhombic crystals melting at 81°, soluble in ether and alcohol, sparingly soluble in water. The *thiocyanate*, $C_4H_3S{\cdot}CO{\cdot}CH_2{\cdot}SCN$, crystallises in colourless leaflets melting at 88°; sparingly soluble in water and light petroleum, readily soluble in chloroform. *Dibromacetothiënone*, $C_4SH_3{\cdot}CO{\cdot}CHBr_2$, is a heavy, colourless oil, solidifying in a freezing mixture, and completely decomposed when heated under ordinary pressure.

Cinnamyl thiënyl ketone, $C_4SH_3{\cdot}CO{\cdot}CH:CHPh$, prepared by saturating with hydrogen chloride a mixture of acetothiënone and benzaldehyde in equimolecular proportions, crystallises in grouped needles or prisms, very soluble in ether and chloroform, sparingly soluble in water. The dibromo-compound crystallises in colourless leaflets melting at 157°, and is soluble in alcohol. V. H. V.

Isomerism of the Thiophenic Acids. Derivatives of β-Thiophenic Acid. By A. Damsky (*Ber.*, **19**, 3282—3286; compare this vol., p. 129).—The ordinary method of preparing β-thiophenic acid by the oxidation of β-thiotolen affording only a poor yield, the author prepared β-ethylthiophen and oxidised it with potassium permanganate; no advantage, however, was derived thereby, since the amount of β-acid obtained was not greater than that formed by the oxidation of β-thiotolen. The best yield, 8 per cent. of the theoretical quantity, was obtained by oxidising β-thiotolen in quantities of 1 gram with a mixture of 6·7 grams of sodium hydroxide, and 3·3 grams of potassium permanganate in 333 grams of water. When dissolved in water at 15° or 18°, 100 c.c. of the solution contain 0·44 gram of β-thiophenic acid; the solubility of the barium salt is 11·54 at 17°, and that of the calcium salt is 7·92 at 14·5°. The *amide* crystallises in slender, colourless needles, melts at 177·5—178°, and is very sparingly soluble in ether; the *phenylcarbamide* crystallises in concentrically-grouped needles, melts at 206°, and is sparingly soluble in alcohol.

β-Ethylthiophen, C_4SH_3Et.—When ethyl ethenyltricarboxylate (Abstr., 1883, 45) is treated with the calculated quantities of sodium ethoxide and ethyl bromide, a vigorous action takes place, accompanied by considerable development of heat, and ethyl butenyltricarboxylate is obtained as an oil. This is saponified, and from the acid, by heating it at 120—170° until evolution of carbonic anhydride ceases, β-ethylsuccinic acid is obtained, which by distillation with phosphorus trisulphide yields β-ethylthiophen. This is an oil resembling α-ethylthiophen in properties. W. P. W.

Reduction of αα-Thiophendicarboxylic Acid. By F. Ernst (*Ber.*, **19**, 3274—3278).—*Tetrahydrothiophendicarboxylic acid*,

$$C_4SH_6(COOH)_2\ [=2:5],$$

is prepared by adding 15 parts of sodium amalgam (4 per cent. Na) to 1 part of α-α-thiophendicarboxylic acid and 0·5 part of sodium hydroxide dissolved in water, and heating at 100° for two hours; the

product is converted into the silver salt, and from this by treatment with hydrogen sulphide the hydro-acid is obtained. It crystallises in yellowish-white probably monoclinic tables, melts at 162° (corr.), is readily soluble in water, less so in ether, and shows all the properties of a hydro-acid. Thus it reduces an ammoniacal silver solution, and when heated with sulphuric acid decomposes into thiophenic acid and carbonic oxide. The *barium* salt, $C_4SH_6(COO)_2Ba$, crystallises in small lustrous scales; and the *silver* salt, $C_4SH_6(COOAg)_2$, is a white powder. When an alcoholic solution of the hydro-acid is saturated with hydrogen chloride, *methyltetrahydrothiophendicarboxylate*,

$$C_4SH_6(COOMe)_2,$$

is obtained as an oil which cannot be distilled and does not solidify.

α-Thiophencarboxylic acid, on reduction, yields an acid which crystallises in colourless needles, melts at about 48°, is readily soluble in water, and reduces ammoniacal silver solution. W. P. W.

Synthetical Investigations in the Thiophen Series. By F. Ernst (*Ber.*, **19**, 3278—3282).—The author has endeavoured to effect the synthesis of an anthracene of the thiophen series, but without success. The following compounds prepared in the course of the work are described:—

Orthotoluyl thiënyl ketone, $C_6H_4Me\cdot CO\cdot C_4SH_3$, obtained by the action of orthotoluic chloride on thiophen in the presence of aluminium chloride, is a colourless oil; when boiled for some time it loses water, and is completely resinified. The *acetoxime* is a non-volatile oil.

Phenyl thiotolyl ketone, $C_6H_5\cdot CO\cdot C_4SH_2Me$, is formed by treating coal-tar thiotolen with benzoic chloride in the presence of aluminium chloride. The ketone is a syrup, and on long boiling loses water and is resinified. The *acetoxime* was prepared, but is not described. When thiënylglyoxylic acid is reduced with sodium amalgam in the cold, *thiënylglycollic acid*, $C_4SH_3\cdot CH(OH)\cdot COOH$, is obtained. It crystallises in white needles, melts at 115°, is readily soluble in water, alcohol, ether and benzene, and decomposes on distillation. Oxidation with manganese dioxide converts it into thiophenaldehyde; the yield, however, is small. The *barium* and *calcium* salts are readily soluble in water; the *silver* salt is obtained as a white precipitate.

Thiënylacetic acid, $C_4SH_3\cdot CH_2\cdot COOH$, is obtained by boiling thiënylglycollic acid with hydriodic acid and amorphous phosphorus. It forms colourless crystals, melts at 76°, and is soluble in hot water, alcohol and ether. The *barium* salt forms white crystals readily soluble in water; the *silver* salt is obtained as a white precipitate.

W. P. W.

Synthesis of α-Phenylthiophen. By W. Kues and C. Paal (*Ber.*, **19**, 3141—3144).—Following out their previous work (Abstr., 1886, 536), the authors find that if β-benzopropionic or β-benzoisosuccinic acid is substituted for levulinic acid, similar reactions occur. In these cases, however, the intermediate hydroxy-product appears to be less stable than thiotolen, and traces only were obtained. The main product was *α-phenylthiophen*, C_4SH_3Ph [Ph = 1]. With the

isosuccinic acid, evolution of carbonic anhydride and formation of the ketonic acid takes place before the reaction occurs. α-Phenylthiophen crystallises in plates melting at 40—41°, and is soluble in carbon bisulphide and the usual organic solvents, insoluble in water. It is volatile in steam, and has the characteristic odour of diphenyl. It dissolves in cold concentrated sulphuric acid, and is reprecipitated unchanged on the addition of water. It shows the indophenin reaction, but does not give any characteristic coloration with Laubenheimer's reaction. When added to cold bromine, it forms *parabromophenyltribromothiophen*, which crystallises in white needles melting at 145—146°, sparingly soluble in alcohol and acetic acid, easily in carbon bisulphide and benzene. It is a very stable compound, may be heated with dilute nitric acid at 180° without change, and is only oxidised by continued boiling with chromic acid in acetic solution, and then forms parabromobenzoic acid. Attempts made to form a phenyltribromothiophen were unsuccessful. A mixture of a compound crystallising in white needles melting at 55—56° (probably a phenyldibromothiophen) with a very soluble bromo-derivative, melting at 33—36°, was produced. L. T. T.

Pentathiophen-group. By K. Krekeler (*Ber.*, **19**, 3266—3274). —The lactone of α-methylhydroxyglutaric acid (Block and Tollens, Abstr., 1886, 533) is prepared by slowly adding 100 grams of levulic acid to 100 grams of potassium cyanide, finely rubbed with 10 grams of water, the whole being well cooled. It is then kept for 24 hours in a loosely-closed vessel, treated with the necessary amount of fuming hydrochloric acid, and left for three or four days. It is extracted with ether, saponified by heating for one hour on a water-bath with fuming hydrochloric acid, and again extracted with ether. It is purified by means of the barium salt. The hydroxy-acid is converted into methylglutaric acid by boiling with twice its volume of hydriodic acid and amorphous phosphorus.

β-Methylpentathiophen, $CH_2<\begin{matrix}CMe:CH\\CH=CH\end{matrix}>S$, is obtained by distilling 5 grams of sodium methylglutarate (dried at 160°) with 10 grams of phosphorus trisulphide at 180—250°. From 550 grams of sodium salt, 20 grams of crude oil were obtained; this is boiled for some hours with strong potash solution, distilled, the oily distillate treated with a little dilute permanganate solution, and then re-distilled over sodium. It is a colourless, very refractive oil, boiling at 134°, and has the odour of pure xylene. Sp. gr. = 0·9938 at 19° (water at 19° = 1). When the solution of the substance in glacial acetic acid is treated with a solution of isatin in the same solvent, and then with sulphuric acid (keeping it cold), an intense dark-green coloration is produced. When poured into water, a green flaky precipitate is formed, soluble in ether. Laubenheimer's reaction yields a dark violet coloration in sulphuric acid.

β-Methylacetopentathiënone, C_5SH_4MeAc, is prepared by treating a solution of 1 part of β-methylpentathiënone in 10 parts of light petroleum with the calculated amount of acetic chloride, and adding aluminium chloride until the evolution of hydrogen chloride ceases.

It is purified by steam distillation. It is a clear heavy oil, having an odour resembling that of acetophenone; it boils at 233—235° (uncorr.). The *ketoxime*, $C_5SH_4Me{\cdot}CMe{:}N{\cdot}OH$, was prepared by Peter's method (Abstr., 1885, 141). It crystallises from ether in long, branched needles melting at 68°; it dissolves readily in alcohol and ether.

When β-methylpentathiophen is treated with 0·3 per cent. alkaline potassium permanganate solution, the oxidation takes place very quickly with formation of acetic and oxalic acids.

When air saturated with methylpentathiophen is passed through fuming nitric acid a nitro-compound is formed. The alcoholic solution of the latter, treated with a drop of potash solution, acquires an intense violet-red colour which disappears in a few minutes.

N. H. M.

Action of Light on Nitrobenzene in Alcoholic Solution. By G. Ciamician and P. Silber (*Ber.*, **19**, 2899—2900).—In continuation of experiments on the transformation of quinone to quinol on exposing its alcoholic solution to sunlight (Abstr., 1886, 695), the authors have studied the chemical change induced in nitrobenzene under similar conditions. Among the products obtained, were aldehyde, aniline, and a quinoline base, probably quinaldine.

V. H. V.

Orthoethyltoluene: Oxidation of Orthodialkyl-derivatives of Benzene with Potassium Permanganate. By A. Claus and E. Pieszcek (*Ber.*, **19**, 3083—3092).—The common statement that ortho-xylene, on oxidation with potassium permanganate, yields first orthotoluic acid and then phthalic acid is incorrect, nothing but phthalic acid being formed; not even a trace of orthotoluic acid is detectable. By the oxidation of orthoethyltoluene with potassium permanganate, orthotoluic, phthalic, and terephthalic acids were obtained according to the temperature and concentration of the solutions. At 100°, in alkaline solution, total combustion took place. The results obtained with cymene completely corresponded with those obtained with orthoethyltoluene.

Bromorthoethyltoluene is a colourless oil boiling at 220—221° (uncorr.); when heated with nitric acid, sp. gr. 1·2, in sealed tubes at 190—200°, it is oxidised to a *bromorthotoluic acid*, [Me : COOH : Br = 1 : 2 : 4]. This forms snow-like flocks composed of slender needles, melts at 118° (uncorr.), is sparingly soluble in cold water, readily soluble in alcohol, ether, and hot water, and yields readily soluble crystalline salts with the alkali metals, and with barium and calcium. It is not identical with the acid described by Jacobsen (Abstr., 1885, 143), to which he assigned the same constitution; the authors consider it more probable that his acid has the constitution [1 : 3 : 4].

By the action of nitric acid on orthoethyltoluene in the cold, a *mono-* and *dinitro*-derivative are formed; the latter is a pale-yellow oil, and does not solidify at 0°.

Orthoethyltoluene-β-sulphonic acid, $C_6H_3MeEt{\cdot}SO_3H$ [1 : 2 : 4], is obtained, together with the α-acid which has not yet been investigated, by the action of pyrosulphuric acid on orthoethyltoluene; it forms a deliquescent, colourless, crystalline mass. The potassium, sodium,

barium, calcium, lead, copper, and silver salts are described. The *chloride* is a yellow oil, the *amide* forms a yellow, buttery mass.

A. J. G.

Oxidation of the Homologues of Phenol. By B. Heymann and W. Königs (*Ber.*, **19**, 3304—3315).—Continuing their experiments (Abstr., 1886, 542), the authors find that the oxidation of the homologues of phenol can readily be effected if the phenols are converted into the corresponding dipotassium phosphates; these double salts are prepared by heating the phenols (1 mol.) with phosphoric oxychloride (1 mol.), carefully adding water to the cooled product, extracting the resulting chlorinated phosphorus compounds with ether, and decomposing them with potassium carbonate. The double phosphates are then oxidised with alkaline potassium permanganate, acidified with hydrochloric acid, and boiled for a short time. The double phosphates of the phenols are found to be more stable than the corresponding double sulphates, and a better yield is obtained when the former are oxidised. By this method, orthocresol is readily oxidised to salicylic acid.

Thymol treated with potassium pyrosulphate yields a double sulphate, $C_6H_3MePr^{\alpha}\cdot SO_4K$ [Me : SO_4K : Pr = 1 : 3 : 4], crystallising in fine silky fibres, which decomposes readily on keeping or when heated on a water-bath, although it is stable in alkaline solution; it is sparingly soluble in 50 per cent. alcohol, readily soluble in absolute alcohol and in water. When the double sulphate or double phosphate is oxidised, thymohydroxycumic acid, $COOH\cdot C_6H_3Pr^{\beta}\cdot OH$ [COOH : OH : Pr = 1 : 3 : 4] (Abstr., 1879, 158), is obtained.

Carvacryl potassium sulphate, $C_6H_3MePr\cdot SO_4K$, crystallises in silvery scales, decomposes very readily on keeping or on gently heating, is stable in alkaline solution, and is soluble in water and absolute alcohol. *Carvacryl dipotassium phosphate*, $C_6H_3MePr\cdot PO_4K_2 + 5H_2O$, crystallises in large, silvery laminæ decomposing at 100°, readily soluble in water and in absolute alcohol. Some tricarvacryl phosphate was formed in the preparation of the double salt. When oxidised with permanganate, both the double sulphate and double phosphate yield *parahydroxyisopropylsalicylic acid*, $COOH\cdot C_6H_3(OH)\cdot CMe_2\cdot OH$ [COOH : OH : $CMe_2\cdot OH$ = 1 : 2 : 4], which crystallises from water in large, flat needles, and in slender, concentrically grouped needles from chloroform. The acid melts at 130—135°; a more exact determination was not possible owing to the tendency to dehydrate and form parapropenylsalicylic acid. Hydroxyisopropylsalicylic acid is sparingly soluble in cold water, readily soluble in chloroform, alcohol and ether, insoluble in carbon bisulphide, and gives with ferric chloride an intense reddish-violet coloration. The *silver* salt, $C_{10}H_{11}O_4Ag$, crystallises in colourless needles; the *copper* salt, $(C_{10}H_{11}O_4)_2Cu + H_2O$, crystallises in green prisms which do not lose their colour on drying; it is sparingly soluble in water. When heated with concentrated hydriodic acid and amorphous phosphorus, the acid is reduced to isohydroxycumic acid, $OH\cdot C_6H_3Pr^{\beta}\cdot COOH$ (Abstr., 1878, 731).

Parapropenylsalicylic acid,

$COOH\cdot C_6H_3(OH)\cdot CMe : CH_2$ [COOH : OH : (CMe : CH_2) = 1 : 2 : 4],

is readily obtained from hydroxyisopropylsalicylic acid by gently warming it on a water-bath with dilute hydrochloric acid. It crystallises in slender needles, melts at 145—146°, is sparingly soluble in cold water, readily soluble in alcohol, ether and boiling carbon bisulphide, and gives an intense reddish-violet coloration with ferric chloride. It is volatile with steam, and when heated at 150° sublimes with slight decomposition. The *silver* salt, $C_{10}H_9O_3Ag$, forms a crystalline powder, very sparingly soluble in water; the *copper* salt, $(C_{10}H_9O_3)_2Cu + 2H_2O$, forms small, green crystals insoluble in water, the anhydrous salt is not hygroscopic. By reduction with sodium amalgam in the cold, an acid agreeing in its properties with Jacobsen's isohydroxycumic acid (*loc. cit.*) was obtained; the melting point, however, was 96—97° instead of 93—94°.

When a boiling aqueous solution of hydroxyisopropylsalicylic acid is treated with an equal volume of concentrated hydrochloric acid, a polymeride, *propenylsalicylic acid*, $(C_{10}H_{10}O_3)_x$, is obtained in small, white crystals which melt at 230° with evolution of carbonic anhydride. It is insoluble in water and carbon bisulphide, soluble in hot acetic acid, alcohol and ether, and the alcoholic solution is coloured an intense reddish-violet with ferric chloride. The acid is not volatile with steam nor is it reduced by sodium amalgam.

Attempts to oxidise the ethyl, isopropyl, isobutyl, and amyl potassium sulphates led to no result. W. P. W.

Action of Sodium Methoxide on Bromobenzene. By F. Blau (*Monatsh. Chem.*, **7**, 621—636).—When bromobenzene is heated with sodium methoxide in sealed tubes, anisoïl is formed together with phenol; the sodium methoxide thus acting like a mixture of the alcohol and alkali: a considerable proportion of the bromobenzene is unaltered. The reactions with di- and symmetrical tri-bromobenzenes are precisely analogous; thus from the former are obtained bromanisoïl, dimethylquinol, and bromophenol; from the latter a dibromophenol and dibromanisoïl. The dibromophenol forms white crystals melting at 76·5°, readily soluble in alcohol and ether, sparingly in water and petroleum; on fusion with alkali, it yields phloroglucol; it is, therefore, a symmetrical compound. V. H. V.

Bisulphides with Mixed Organic Radicles. By R. Otto and A. Rössing (*Ber.*, **19**, 3132—3138).—Hitherto no organic bisulphides with mixed radicles have been obtained. The authors find that such compounds are formed when a mixture of two mercaptans are treated with bromine, and that the reactions take place the more readily the more closely allied are the radicles of the reacting mercaptans. The reaction is $R{\cdot}SH + R'{\cdot}SH + Br_2 = 2HBr + R{\cdot}S_2{\cdot}R'$.

Phenyl paratolyl bisulphide, $C_7H_7{\cdot}S_2{\cdot}Ph$, is obtained by dissolving molecular proportions of phenyl and paratolyl hydrosulphides in ten times their volume of ether, and slowly adding a molecular proportion of bromine. This substance is a thick, pale-yellow oil. It is insoluble in water, miscible in all proportions with alcohol and ether, has an odour somewhat resembling that of tolyl hydrosulphide, is heavier than water, and scarcely volatile in steam. When heated with alcohol and zinc-dust, it is decomposed into the corresponding zinc mercaptides.

Ethyl amyl bisulphide, prepared in a similar way, is a thin, colourless liquid of very strong and unpleasant garlic-like odour. It is insoluble in water, soluble in ether and alcohol, lighter than water, and volatile in steam.

Ethyl phenyl bisulphide.—The authors attempted to obtain this compound by the above method, but it was only formed in very small quantity, the principal products being diethyl and diphenyl bisulphides. But by modifying Schiller and Otto's method for the preparation of organic bisulphides (this Journal, 1877, i, 306), the authors were successful. 10 grams of phenylsulphinic acid (1 mol.) and 15 grams of ethyl mercaptan (3 mols.) in alcoholic solution were heated in sealed tubes at 100°. The action took place according to the equation $PhSO_2H + 3EtSH = PhS_2{\cdot}Et + Et_2S_2 + 2H_2O$. Ethyl phenyl bisulphide is a thick, oily, strongly refractive liquid, heavier than water, and only very slightly volatile in steam. It is insoluble in water, soluble in ether and alcohol. Phenyl paratolyl bisulphide was also prepared by the action of phenyl hydrosulphide on paratolylsulphinic acid.

When the ethyl salts of the thiosulphonic acids are heated with mercaptans reactions similar to the above occur; these are not, however, of so simple a kind, but take place simultaneously according to the two equations:—

$$\text{I. } R{\cdot}SO_2{\cdot}SR + 4R'{\cdot}SH = R_2S_2 + 2R'_2S_2 + 2H_2O.$$
$$\text{II. } R{\cdot}SO_2{\cdot}SR + 4R'{\cdot}SH = 2R{\cdot}S_2{\cdot}R' + R'_2S_2.$$

Phenyl disulphoxide ($Ph{\cdot}S_2O_2{\cdot}Ph$) and ethyl mercaptan thus yield ethyl bisulphide, phenyl bisulphide, and ethyl phenyl bisulphide.

L. T. T.

Action of Silicon Fluoride on Organic Bases. By C. L. Jackson and A. M. Comey (*Ber.*, **19**, 3194—3195).—The authors intend studying these reactions. When silicon fluoride is passed over aniline, a compound of the formula $3NH_2Ph,2SiF_4$ is formed. This compound was obtained by Laurent and Delbos (*Ann. Chim. Phys.*, **22**, 101), but its composition was not established. It forms white, microscopic needles, and sublimes without fusion. It is insoluble in ether, benzene, and light petroleum. With water or alcohol, it forms aniline hydrosilicofluoride.

Ortho- and para-toluidine, diphenylamine, and dibenzylamine form similar compounds. L. T. T.

Aniline and Diphenylamine from Phenol. By V. Merz and P. Müller (*Ber.*, **19**, 2901—2917).—In this paper, the various methods used, and the conditions required for the conversion of phenol into aniline and diphenylamine are fully described. Thus when phenol and ammonium zinc chloride or simply ammonium chloride are heated at 330°, 70 to 80 per cent. of the phenol is converted into the amine, the yield of which is dependent on an excess of the ammonium salt, the temperature, and the time of heating. The same change may also be effected with zinc oxide or magnesia and ammonium chloride, the presence of an excess of the latter preventing the formation of diphenylamine. Experiments in an autoclave were not so satisfactory;

the pressure when the mixture was heated at 320°, was 20 to 25 atmospheres. V. H. V.

Action of Alcoholic Hydrogen Chloride on Nitrosamines. By O. Fischer and E. Hepp (*Ber.*, **19**, 2991—2995).—The authors find that certain nitrosamines undergo intramolecular change by the action of alcoholic hydrogen chloride thus; for example, methylphenylnitrosamine is converted into 1 : 4 nitrosomethylaniline.

1 : 4 *Nitrosmethylaniline* is prepared by adding alcoholic hydrogen chloride to an ethereal solution of methylphenylnitrosamine; a vigorous action takes place after some time, and small yellow needles of the 1 : 4 nitrosomethylaniline hydrochloride separate in an almost pure state. The base is obtained by precipitation with sodium carbonate or ammonia, either in yellowish-green laminæ, or from very dilute solutions in large, steel-blue prisms; it is readily soluble in alcohol, ether, and chloroform, sparingly soluble in benzene, and only slightly soluble in light petroleum and in water. It melts at 118° and suffers decomposition when more strongly heated. When heated with solution of sodium hydroxide, it is decomposed into 1 : 4 nitrosophenol and methylamine; whilst by reduction methylparaphenylenediamine is obtained. Paranitrosomethylaniline is a secondary base, and by the action of nitrous acid yields 1 : 4 *nitrosomethylphenylnitrosamine*, $NO{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$; this compound crystallises from alcohol in nodules, and melts at 101°. Careful oxidation with nitric acid of sp. gr. = 1·13 converts it into 1 : 4 *nitromethylphenylnitrosamine;* this forms yellow needles melting at 104°.

When methylaniline, dissolved in alcoholic hydrogen chloride, is treated in the cold with one molecular proportion of sodium nitrite, there separate after long standing two compounds, 1 : 4 nitrosomethylaniline hydrochloride and 1 : 4 nitrosomethylphenylnitrosamine, the latter being formed in the greater quantity, and a corresponding proportion of the methylaniline remaining unacted on.

1 : 4 *Nitrosoethylaniline*, obtained in a manner similar to the methyl-derivative, crystallises in green laminæ, melts at 78°, and is readily soluble in alcohol, ether and benzene, sparingly soluble in water. Its *hydrochloride* crystallises in stellate groups of needles. By reduction, *ethylparaphenylendiamine* is obtained; this base is a thick oil and distils at 270°. Its *hydrochloride* forms colourless, narrow scales readily soluble in water, less soluble in alcohol. From 1 : 4 nitrosoethylaniline, 70 per cent. of the nitrosophenol and 80 per cent. of the ethylamine hydrochloride required by theory were obtained by heating it with sodium hydroxide solution.

1 : 4 *Nitrosoethylorthotoluidine* melts at 140° and crystallises in green scales, frequently exhibiting a bluish shimmer.

1 : 4 *Nitrosodiphenylamine*, obtained from Witt's diphenylnitrosamine, crystallises in green tables showing a bluish shimmer, melts at 143°, and dissolves readily in alcohol, ether, and chloroform, giving brown solutions, and in sulphuric acid with a red colour, which at once changes to violet on warming. The *hydrochloride* crystallises in brown tables having a bronze lustre, or in dark reddish-brown needles, and is decomposed by water with liberation of the base. W. P. W.

Preparation of Benzylamine and Phenethylamine. By S. Hoogewerff and W. A. Van Dorp (*Rec. Trav. Chim.*, **5**, 252—254).—Hofmann has suggested the action of bromine on phenylacetamide in presence of dilute alkali as a convenient method for the preparation of benzylamine (Abstr., 1886, 45). It is here shown that the yield is considerably increased by preparing the alkaline hypobromite first and then adding it subsequently to the amide.

The preparation of benzylamine and phenethylamine by this method is described. V. H. V.

Isodinitrodimethylaniline. By P. v. Romburgh (*Rec. Trav. Chim.*, **5**, 240—245).—According to Mertens, when dinitrophenylnitramine is heated with phenol, tetranitrodimethylazobenzene, a red compound is produced, reconvertible into the nitramine by treatment with nitric acid (Abstr., 1885, 1022). As, however, trinitrophenylmethylnitramine yields a similar red substance, reconvertible into the nitramine, which has been shown to be trinitrophenylmethylaniline, it is probable that the red substance obtained by Mertens is a dinitromethylaniline. The analytical results support this view quite as well as that of Mertens. As a confirmation, the author by acting on tetramethylbenzidine with nitric acid, obtained a product resembling the isodinitrodimethylaniline of Mertens, which when boiled with nitric acid yielded the corresponding nitramine; from this, the red substance was obtained, the analysis of which showed that it was a tetranitrodimethylbenzidine. When treated with nitric acid, this yielded the theoretical quantity of the nitramine. V. H. V.

New Synthesis of Thiodiphenylamine. By A. Bernthsen (*Ber.*, **19**, 3255—3256).—Thiodiphenylamine is obtained by heating orthamidophenyl mercaptan and catechol at 220—240° for about 30 hours. The product is extracted with alkali and acid, and crystallised from ether and light petroleum. This synthesis forms an important support in favour of thiodiphenylamine being a di-ortho-compound (compare Bernthsen, Abstr., 1886, 53, and Möhlau, *Ber.*, **19**, 2013).

N. H. M.

Ethereal Carbonates. By G. Bender (*Ber.*, **19**, 2950—2952).—Oxycarbimidophenol, described by Kalckhoff (Abstr., 1883, 1169) and previously by Groenvik (*Bull. Soc. Chim.*, **25**, 177), and hydroxymethenylamidophenol, prepared by Sandmeyer (this vol., p. 135), are identical with the author's anhydro-orthamidophenyl carbonate (Abstr., 1887, 37) which melts at 137—138°. Kalckhoff's compound on further purification becomes white, and its acetyl-derivative is soluble in water like the corresponding substance obtained by the author. The ethyl salt prepared by Sandmeyer has the formula $C_6H_4<^{N}_{O}>C\cdot OEt$, that of the salt obtained by the author is $C_6H_4<^{NEt}_{-O-}>CO$. In the existence of these two isomerides, the parent substance exhibits a remarkable analogy to carbostyril and isatin; it also has a pseudo-form in addition to its ordinary

one, although whether the latter is a lactim or lactam cannot yet be decided.

The author's ethyl salt melts at 29° and has a bitter taste. Concentrated hydrochloric acid is without action on it at 100°, but dissolves it in the cold forming a highly unstable hydrochloride.

W. P. W.

Benzyl-derivatives of Hydroxylamine. By F. Walder (*Ber.*, **19**, 3287—3294).—Further investigation has shown that the conclusions respecting the composition of these compounds arrived at in the author's previous paper (Abstr., 1886, 796) are erroneous. A complete analysis of the compound obtained by the action of methyl iodide and sodium on dibenzylhydroxylamine and described as tribenzylbenzoxyammonium iodide, shows that it has the formula $N_2(C_7H_7)_4O,HI$. The hydriodide can be decomposed by alkalis, but, since the base is soluble in water and only sparingly soluble in ether, a separation is better effected by employing moist silver oxide. The base crystallises over sulphuric acid, distils with decomposition at high temperatures, and is very deliquescent; when heated with water, it yields dibenzylhydroxylamine, whilst by the action of acetic anhydride acetyldibenzylhydroxylamine is obtained. The *platinochloride*, $N_2(C_7H_7)_4O,H_2PtCl_6$, crystallises in slender, yellow needles, melts at 153°, and is insoluble in cold water and ether. The *sulphate*, $N_2(C_7H_7)_4O,H_2SO_4$, forms transparent prisms, melts at 152°, and is insoluble in alcohol and ether, readily soluble in water containing acid. The *nitrate*, $N_2(C_7H_7)_4O,2HNO_3$, crystallises in white, feathery, flat needles, melts at 159°, and is sparingly soluble in water. The *hydrochloride*, $N_2(C_7H_7)_4O,2HCl$, forms thick prisms showing a nacreous lustre, is insoluble in ether, and only sparingly soluble in water after it has once separated from solution. A second *hydriodide*, $N_2(C_7H_7)_4O,2HI$, crystallises in bright yellow aggregates, melts at 27°, and is soluble in alcohol.

From a black, resinous mass formed in the preparation of the hydriodide, $N_2(C_7H_7)_4O,HI$, a black, crystalline compound may be obtained; it appears to be a periodide of the formula $N_2(C_7H_7)_4O,MeI,I_2$.

The base previously described as benzylbenzenylamine proves to be *dibenzylamine*, $NH(C_7H_7)_2$. It is found that when dibenzylhydroxylamine is heated with phosphorus trichloride and the product extracted with dry ether, an unstable, bright-yellow viscid oil containing phosphorus and chlorine is obtained, which on addition of water yields dibenzylamine. The *nitrosamine*, $(C_7H_7)_2N{\cdot}NO$, forms brittle, curved, white crystals, melts at 61°, and is readily soluble in alcohol, ether and light petroleum, insoluble in water. The *platinochloride*, $N(C_7H_7)_2H,H_2PtCl_6$, crystallises in golden-yellow needles; the *nitrate*, $N(C_7H_7)_2H,HNO_3$, crystallises in slender glistening needles, melts at 186°, and is sparingly soluble in water. When heated with benzyl chloride at 100°, the base is converted into tribenzylamine.

When dibenzylhydroxylamine hydrochloride is treated with potassium nitrite in the cold, *nitrosodibenzylhydroxylamine*, $N(C_7H_7)_2O{\cdot}NO$, is obtained; this crystallises in flat, white needles, melts at 82—84°,

and is soluble in alcohol and ether, sparingly soluble in light petroleum, insoluble in water. If, however, cooling be omitted, and the nitrate be added rapidly to the hydrochloride, *nitrosodibenzylamine* is obtained, $N(C_7H_7)_2OH + 2HNO_2 = HNO_3 + H_2O + N(C_7H_7)_2{\cdot}NO$.

The author finds that mono-, di-, and tri-benzylamine are also formed when dibenzylhydroxylamine is prepared by Schramm's method (Abstr., 1884, 51). W. P. W.

Correction. By L. Knorr (*Ber.*, **19**, 3303).—In a previous paper (Abstr., 1884, 1198), a compound, $C_{14}H_{16}N_2O_4$, was stated to have been obtained by the action of ethyl acetoacetate on orthophenylenediamine, instead of on paraphenylenediamine. Sulphuric acid is without action on the compound in the cold, but at 100° paraphenylenediamine is eliminated. W. P. W.

Action of Ethyl Acetoacetate on Aromatic Diamines. By O. N. Witt (*Ber.*, **19**, 2977—2978 and 3299).—By the action of ethyl acetoacetate on orthotoluylenediamine, ethenyltoluylenediamidine is formed. This confirms the results obtained by Ladenburg and Rügheimer (Abstr., 1879, 915), the priority of whose work is acknowledged by the author in the second communication.

Condensation Products from Carbo-imides and Orthodiamines. By C. Dahm and K. Gasiorowski (*Ber.*, **19**, 3057—3060).—*Carborthotoluylenediphenyltetramine*, $C_7H_6{<}\overset{NH}{NH}{>}C(NHPh)_2$, is prepared by heating carbodiphenylimide and orthotoluylenediamine (molecular weights) for four hours at 130—140°. It crystallises from benzene in needles melting at 161°, and is readily soluble in alcohol and ether. It does not react with an excess of imide. The *hydrochloride*, $2C_{20}H_{20}N_4,3HCl$, crystallises in white needles melting at 173—174°; it is very soluble in alcohol and ether, rather sparingly in water. The *sulphate* was also prepared.

Carborthotoluylenediparatolyltetramine, $C_{22}H_{24}N_4$, is prepared in a manner similarly to the above-mentioned compound. The product is extracted with boiling benzene, and the white powder dissolved in alcohol, from which it separates in needles melting at 196°. The *hydrochloride*, $2C_{22}H_{24}N_4,3HCl$, crystallises from the strong acid solution in needles melting at 143°. N. H. M.

Derivatives of Parachlorazobenzene. By E. Mentha and K. Heumann (*Ber.*, **19**, 2970—2974; comp. Abstr., 1886, 874).—*Chlorodiamidodiphenyl*, $NH_2{\cdot}C_6H_4{\cdot}C_6H_3Cl{\cdot}NH_2$.—When parachlorazobenzene in alcoholic solution is treated with zinc chloride and sulphuric acid, and the solution, after precipitating the zinc with hydrogen sulphide, is made alkaline with caustic soda, chlorodiamidodiphenyl is obtained and can be extracted with ether. It is a bright yellow powder, which very readily becomes oxidised. The *hydrochloride*, $C_{12}H_{11}N_2Cl,2HCl$, crystallises in tufts of white needles.

Paranitrochlorazobenzene, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4Cl$ [4 : 1 : 4], is prepared by treating parachlorazobenzene with fuming nitric acid. It forms slender, pale-yellow needles, melts at 132·5°, and is insoluble in water, sparingly soluble in cold alcohol and ether, readily soluble in acetic acid.

Parachlorazobenzenesulphonic acid, $SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4Cl$, [4 : 1 : 4], is obtained by heating parachlorazobenzene with 10 per cent. fuming sulphuric acid at 60—70° for some time. It crystallises in brown needles, melts at 148°, and is very soluble in water and alcohol. The *sodium* and *barium* salts are described. The *chloride*, $C_{12}H_8N_2Cl \cdot SO_2Cl$, melts at 130°, and crystallises in glistening, red prisms, soluble in alcohol and ether; boiling with water converts it into the acid. The *amide* forms brownish-yellow prisms, melts at 211°, and is insoluble in water, sparingly soluble in ether and cold alcohol. W. P. W.

Cyanazobenzene and Parazobenzenecarboxylic Acid. By E. Mentha and K. Heumann (*Ber.*, **19**, 3022—3025).—*Paracyanazobenzene*, $C_{13}H_9N_3$, is prepared by slowly adding a solution of diazobenzene chloride (from 40 grams of amido-azobenzene hydrochloride) to a solution of copper sulphate (100 grams) and potassium cyanide (90 per cent., 112 grams) in 600 c.c. of water at 90°. When cold, it is filtered, well washed, and dried; it is then sublimed and recrystallised from benzene, from which it separates in short brown needles. It melts at 100—101°, is insoluble in water, readily soluble in warm alcohol, ether, and benzene.

Parazobenzenecarboxylic acid, $NPh : N \cdot C_6H_4 \cdot COOH$, is obtained by boiling the above nitrile in the pure state for three hours with concentrated aqueous potash. It crystallises from alcohol in long, lustrous, brown prisms, soluble in ether and warm benzene. When heated above 210°, it becomes dark, and decomposes at a higher temperature. When heated with lime, a sublimate is obtained which melts at 170—171°, and is probably azophenylene. The *potassium salt* crystallises in brownish-yellow needles soluble in water and in alcohol; the *barium salt* forms needles sparingly soluble in water, rather readily soluble in alcohol. Several other salts were prepared. N. H. M.

Chloroparazotoluene. By E. Mentha (*Ber.*, **19**, 3026).—*Chloroparazotoluene*, $C_{14}H_{13}N_2Cl$, is prepared by treating 4·5 grams of amidoparazotoluene (obtained by Nölting and Witt's method, Abstr., 1884, 742) with 200 c.c. of water and 150 c.c. of strong hydrochloric acid, and adding a solution of 5 grams of cuprous chloride in 45 c.c. of hydrochloric acid. It is then heated to 90°, and a solution of 2·5 grams of sodium nitrite in 25 c.c. of water gradually added. The product is filtered, treated with hydrochloric acid and with soda solution, and ultimately crystallised from alcohol. It forms brown plates which melt at 97°, dissolves readily in ether, alcohol, and benzene, and closely resembles parachlorazobenzene (compare Abstr., 1886, 874). N. H. M.

Reduction of Aldoximes and Acetoximes. By H. Goldschmidt (*Ber.*, **19**, 3232—3234).—*Carvylamine*, $C_{10}H_{17}N$, is obtained by reducing carvoxime in alcoholic solution with sodium amalgam in presence of acetic acid.

Benzylamine can be conveniently prepared by gradually adding 160 grams of $2\frac{1}{2}$ per cent. sodium amalgam to a solution of 5 grams of benzaldoxime in 20 c.c. of alcohol at 50—60°; the solution must be kept acid by addition of acetic acid. It is poured into water, saturated with ether, made alkaline, and again extracted with ether. The ethereal extract is dried, and treated with hydrogen chloride; benzylamine hydrochloride then separates as a white precipitate. Benzhydrylamine and isobutylamine were prepared in a similar manner from benzophenoxime and isobutylaldoxime respectively.

N. H. M.

Pyrogenic Formation of Phenazine. By A. Bernthsen (*Ber.*, **19**, 3256—3258).—The author succeeded in isolating phenazine from the product obtained by passing aniline through a red-hot tube (Abstr., 1886, 471). The product was repeatedly exhausted with moderately dilute hot hydrochloric acid, the brown solution precipitated with ammonia, extracted with ether, and the ethereal solution shaken several times with dilute hydrochloric acid. In this way, the stronger bases were dissolved, but not the phenazine. The ether was distilled off, the residue extracted with hot dilute hydrochloric acid, filtered when cold, and precipitated with ammonia. It was then sublimed, and the lustrous, yellow needles identified as phenazine. This pyrogenic formation of phenazine corresponds with that of anthracene from toluene.

N. H. M.

Safranine Dyes. By R. Nietzki (*Ber.*, **19**, 3017—3022).—Previous experiments (Abstr., 1883, 731) made it probable that safranine contains two amido-groups, and that the third nitrogen-atom is tertiary or quaternary.

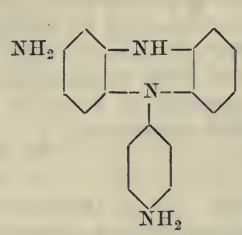
When phenosafranine, $C_{18}H_{14}N_4$, is boiled with alcohol, sulphuric acid, and sodium nitrite, the compound $C_{18}H_{13}N_3$ is formed. This is a dye of a bluer shade than safranine, from which it is also distinguished by the absence of fluorescence of its alcoholic solution and in its behaviour towards strong sulphuric acid:—safranine dissolves with a green colour, which changes to blue and red on addition of water; the new compound dissolves, yielding a yellowish-brown solution, which when diluted becomes first green and then red. The *monacetyl-derivative* is violet, and yields crystalline, yellow salts.

The second amido-group in safranine can be removed only with difficulty, and in strongly acid solution. A reddish-violet base was obtained, which yields brownish-yellow salts. It shows the same reactions as the acetyl-derivatives of safranine.

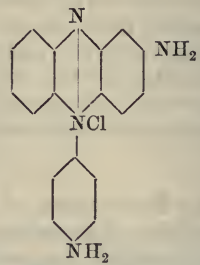
The two constitutional formulæ for safranine lately proposed by Bernthsen (this vol., p. 139) are shown by the author to be incorrect. With the one, the existence of the two isomeric diethylsafranines obtained by the author (*loc. cit.*) cannot be accounted for; the other formula permits the existence of the two isomerides, but only one of

the latter could be diazotised. It has been shown that both the diethylsafranines very readily yield diazo-compounds. N. H. M.

Constitution of the Safranines. By O. N. Witt (*Ber.*, **19**, 3121—3124).—The author criticises the constitution assigned to the phenosafranines by Andresen (Abstr., 1885, 1026) and by Bernthsen (this vol., p. 139), and suggests the following:—



Leucosafranine.



Phenosafranine hydrochloride.

A. J. G.

Constitution of Safranine. By R. Nietzki (*Ber.*, **19**, 3163—3166).—The author supports the correctness of the formulæ suggested by Witt (see preceding Abstract). O. Lehmann has examined crystallographically the nitrates of the two dimethylsafranines previously described by the author, and the non-identity of which has been lately called in question by Bernthsen (this vol., p. 139). Lehmann declares the two compounds to be undoubtedly different.

The author has carried out the idea mentioned in his last paper on this subject, and tested the safranine-forming power of the six isomeric xylidines, $C_6H_3Me_2{\cdot}NH_2$, and of the three isomeric compounds ($C_6H_2Me_3{\cdot}NH_2$) cumidine, mesidine, and isocumidine when heated with paradiamidodiphenylamine. The results—taking NH_2 as always occupying the position 1—may be expressed as follows:—The xylidines 1 : 3 : 4 and 1 : 2 : 4 gave safranine; 1 : 2 : 5, 1 : 2 : 6, and 1 : 3 : 5 gave no safranine; and 1 : 2 : 3 gave only traces, which were probably due to traces of the 1 : 3 : 4 compound present as impurity in the xylidine used. Ordinary cumidine, [1 : 2 : 4 : 5], gave a safranine, whilst mesidine, [1 : 2 : 4 : 6], and isocumidine, [1 : 3 : 4 : 5], gave none. It is therefore clear that the position of the methyl-groups in the monamine plays a determining part in the formation or non-formation of safranines.

The author considers that Witt's formula is much more in harmony with the above and other facts known about safranine than is either Andresen's or Bernthsen's formula. L. T. T.

Paranitroformanilide. By T. B. Osborn and W. G. Mixter (*Amer. Chem. J.*, **8**, 346—347).—This substance, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COH$, was prepared by adding formanilide to fuming nitric acid, sp. gr. 1·53, in a freezing mixture, and pouring the product into cold water; it was washed with water and ether, then crystallised from alcohol. It

melts at 187° or 194°, according as it has been crystallised from alcohol or from hot water. When boiled with caustic potash, it yields paranitraniline. Attempts to obtain azo-compounds by its reduction were unsuccessful. H. B.

Orthazoparabromacetanilide. By C. H. Matthiessen and W. G. Mixter (*Amer. Chem. J.*, **8**, 347—349).—Parabromacetanilide was converted into orthonitroparabromacetanilide and then treated in warm alcoholic solution with zinc and strong aqueous ammonia for half an hour. The red precipitate was washed with water, dilute acid, and alcohol. During the reduction, a portion of the bromine is displaced with formation of azoacetanilide, which is only removed by heating with concentrated hydrochloric acid at 100°. The product thus purified is *orthazoparabromacetanilide*, $N_2(C_6H_3Br{\cdot}NHAc)_2$. It is a pale red substance melting at 280—282°, and is acted on by potash with great difficulty. H. B.

Halogen-derivatives of Oxanilide. By J. O. Dyer and W. G. Mixter (*Amer. Chem. J.*, **8**, 349—357).—*Tetrachloroxanilide*,

$$C_2O_2(NH{\cdot}C_6H_3Cl)_2\ [1:2:4],$$

is obtained by passing chlorine into an acetic acid solution of oxanilide. It separates in slender, white fibres melting at about 255°, and is difficult to obtain quite pure. On decomposition, it yields metadichloraniline, melting at 63°.

Paradibromoxanilide, $C_2O_2(NH{\cdot}C_6H_4Br)_2$, is obtained by adding bromine in excess to a boiling acetic acid solution of oxanilide. It melts above 300°. Treated with alcoholic potash, it yields parabromaniline.

Paradiiodoxanilide is prepared by the action of iodine and strong nitric acid; crystallised from aniline it is quite white. It decomposes before melting. Treated with potash it yields paraiodaniline.

Boiling alcoholic potash converts oxanilide into oxanilic acid, and then into oxalic acid and aniline. The substituted oxanilides behave similarly. *Metadichloroxanilic acid*, $C_6H_3Cl_2{\cdot}NH{\cdot}CO{\cdot}COOH$, is formed along with metadichloraniline by the hydrolysis of the tetrachloroxanilide. It dissolves in 808 parts of water at 25° and melts at 122°; the potassium salt crystallises from hot water in fine fibres.

Parabromoxanilic acid, $C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}COOH$, is readily soluble in hot water, and in 515 parts of water at 25°; it melts at 198°. The potassium salt is anhydrous, and forms tabular, monoclinic crystals; the calcium, barium, and silver salts are also anhydrous, and sparingly soluble in water. *Paraiodoxanilic acid*, $C_6H_4I{\cdot}NH{\cdot}CO{\cdot}COOH$, melts with decomposition at 197—200°, and dissolves in 1385 parts of water at 25°; the potassium salt is anhydrous. H. B.

Action of Concentrated Sulphuric Acid on Aromatic Ketones. By A. Claus (*Ber.*, **19**, 2879—2881).—In this paper, preliminary experiments are described on the decomposition of aromatic ketones by fuming sulphuric acid. The reaction consists in the decomposition of the ketone and formation of a carboxylic acid and a sulphonic acid: thus mesityl phenyl ketone yields mesitylsulphonic and benzoic acids. It is proposed to carry on a series of investiga-

tions to determine in the case of mixed ketones containing a simple and a replaced phenyl-group, whether in all cases the former remains combined with the carbonyl grouping and the latter yields the sulphonic acid, as also to investigate the changes produced in the case of a ketone containing the substituted phenyl groupings of differing degrees of complexity. At a low temperature, a sulphonic acid of the ketone is formed; thus barium salts of mesitylphenylketonemonosulphonic and para-xylylphenylketonedisulphonic acids are described.

V. H. V.

Aromatic Ketones. By O. Pampel and G. Schmidt (*Ber.*, **19**, 2896—2899).—*Phenyl ethyl ketone* (propiophenone), COEtPh, is conveniently prepared by Friedel and Crafts' aluminium chloride reaction. Its acetoxime- and phenylhydrazine-compounds are colourless oils; with bromine, it yields a monobromo-derivative as a dark oil, which gives an anilide, $COPh\cdot C_2H_4\cdot NHPh$, separating in yellow, glistening crystals melting at 38°; its acetyl-derivative crystallises in colourless needles melting at 103°.

Naphthyl methyl ketone, $C_{10}H_7\cdot COMe$, prepared by aid of the aluminium chloride reaction, is a pale-yellow oil boiling at 296—299°. Its acetoxime- and phenylhydrazine-derivatives are crystalline compounds melting at 101° and 146° respectively. Its *anilide*,

$$C_{10}H_7\cdot CO\cdot CH_2\cdot NHPh,$$

separates in golden-red crystals melting at 130°; its thiocyanate crystallises in micaceous crystals.

V. H. V.

Benzene-derivatives of High Molecular Weight. By F. Krafft (*Ber.*, **19**, 2982—2988).—*Pentadecylphenyl ketone*, $C_{15}H_{31}\cdot COPh$, is obtained by gradually adding aluminium chloride ($1\frac{1}{2}$ parts) to a cooled solution of palmitic chloride (1 part) in benzene (2 parts) and afterwards gently warming; the product is poured into water, excess of benzene removed by distillation, and by fractional distillation under 15 mm. pressure the ketone is approximately separated from the regenerated palmitic acid, the last traces of which are removed from an alcoholic solution of the distillate by precipitation as barium palmitate. The ketone crystallises in large, glistening laminæ, melts at 59°, boils at 250·5—251° under 15 mm. pressure, and is very sparingly soluble in cold alcohol, soluble in ether and hot alcohol. On oxidation with chromic acid, it yields benzoic and pentadecylic acids.

Hexadecylbenzene, $C_{16}H_{33}Ph$, is prepared by the action of sodium on a mixture of cetyl iodide and iodobenzene. It crystallises in glistening tables, which subsequently become opaque, melts at 27°, and boils at 230° under 15 mm. pressure. When dissolved in fuming sulphuric acid, hexadecylbenzene yields a *monosulphonic acid*, and by fusing its sparingly soluble sodium salt with potassium hydroxide at 250°, *hexadecylphenol*, $C_{16}H_{33}\cdot C_6H_4\cdot OH$, is obtained. This is a colourless, odourless and tasteless compound, melting at 77·5°, and boiling at 260—261° under 16 mm. pressure. *Hexadecylnitrobenzene* is a crystalline powder, melts at 35—36°, and when reduced yields *hexadecylamidobenzene*, which melts at 53°, and distils without decomposition at 254—255° under 14 mm. pressure;

its *platinochloride*, $(C_{16}H_{33}\cdot C_6H_4\cdot NH_2)_2,H_2PtCl_6$, is soluble in ether and alcohol.

Octadecylbenzene, $C_{18}H_{37}Ph$, is obtained by the action of sodium on a solution of octadecyl iodide and iodobenzene in benzene. It forms either an oil which soon solidifies, or crystallises in colourless, odourless and tasteless, silvery scales, melts at 36°, and boils at 249° under 15 mm. pressure. *Octadecylbenzenesulphonic acid* is prepared by treating octadecylbenzene with fuming sulphuric acid and gently warming; the sodium salt when heated with eight times its weight of potassium hydroxide at 250—270° for 10 to 12 hours, yields *octadecylphenol*, $C_{18}H_{37}\cdot C_6H_4\cdot OH$, almost quantitatively. This crystallises in glistening laminæ, melts at 84°, and boils without decomposition at 277° under 15 mm. pressure. Octadecylbenzene is converted by fuming nitric acid into an almost colourless *mononitro*-compound melting at about 48°; by reduction, this yields *octadecylamidobenzene*, which melts at about 61°, and boils at 274° under 15 mm. pressure.

Hexyldiphenylmethane, $C_6H_{13}\cdot CHPh_2$, is formed when 0·2 part of aluminium chloride is slowly added to 1 part of œnanthylidene chloride dissolved in 4 parts of benzene; after standing for two days, the whole is heated at 30° for a short time. It melts at 14°, and boils at 186° under 10 mm., or 193° under 15 mm. pressure. By the action of nitric acid, *hexyldinitrodiphenylmethane*, $C_6H_{13}\cdot CH(C_6H_4\cdot NO_2)_2$, is obtained, and this on reduction yields *hexyldiamidodiphenylmethane*. *Hexyltetramethyldiamidodiphenylmethane* can be prepared either from the latter, or by the condensation of œnanthaldehyde and dimethylaniline with zinc chloride. It melts at 59·5°, boils at 272—278°, and yields a *platinochloride*, $C_{23}H_{34}N_2,H_2PtCl_6$, sparingly soluble in water and ether-alcohol.

When a larger proportion of aluminium chloride is added to œnanthylidene chloride in benzene, *heptylbenzene*, $C_7H_{15}Ph$, is obtained. It boils at 108—110° under 10 mm. pressure. The corresponding *hexyl phenyl ketone*, $C_6H_{13}\cdot COPh$, is prepared by the action of 0·5 part of aluminium chloride on 1 part of heptoic chloride in 2—3 parts of benzene. It melts at 17°, boils at 155° under 15 mm. pressure, and yields an *acetoxime*, which melts at 55°, and crystallises from alcohol in stellate groups of needles. By the action of zinc chloride on heptoic chloride and dimethylaniline, a base, melting at 72·5° and boiling at 278° under 15 mm. pressure, is obtained together with *hexyl dimethamidophenyl ketone*, $C_6H_{13}\cdot CO\cdot C_6H_4\cdot NMe_2$. The ketone melts at 48·5°, boils at 190° under 20 mm. pressure, and yields an *acetoxime*, which crystallises in silvery glistening scales.

W. P. W.

Paraxylyl Ethyl Ketone and its Oxidation to Orthometadimethylbenzoylacetic Acid. By A. Claus and E. Fickert (*Ber.*, **19**, 3182—3184).—*Paraxylyl ethyl ketone*, $C_6H_3Me_2\cdot COEt$, obtained from paraxylene and propionyl chloride, is a colourless, mobile, highly refractive liquid having an aromatic odour and strong bitter taste. It is lighter than water, and boils at 237—238° (uncorr.). When oxidised with dilute solution of potassium permanganate, it yields a mixture of xylylcarboxylic acid and *paraxylyl-β-ketonic* (*orthometadimethylbenzoyl acetic*) *acid*, $C_6H_3Me_2\cdot CO\cdot CH_2\cdot COOH$. The acids are best separated

by means of their barium salts, the ketonate being very sparingly soluble. The ketonic acid is sparingly soluble in water and light petroleum, easily in alcohol, ether, benzene, &c. It crystallises in needles melting at 132° (uncorr.). The *sodium* salt (with $1H_2O$) is easily, the *calcium* ($+ 2\frac{1}{2}H_2O$), *barium* ($+ 4H_2O$), and *silver* salts very sparingly soluble.

Similar reactions have been obtained with aromatic ketones containing the ethyl and propyl, &c., groups, and are now being investigated.

L. T. T.

Nitrophenyl Benzoates and Nitrobenzoates and their Products of Decomposition. By G. Neumann (*Ber.*, **19**, 2979—2982).—Continuing his previous work (Abstr., 1886, 350, 939), the author prepared *metanitrophenyl benzoate* by heating metanitrophenol with benzoic chloride. It is readily soluble in acetic acid, alcohol and hot light petroleum, and forms pale yellow crystals, which melt at 95°. When treated with nitric acid of sp. gr. 1·48, it yields *metanitrophenyl metanitrobenzoate*. This compound forms white crystals, melts at 129°, and is readily soluble in cold chloroform and hot alcohol, ether, and light petroleum.

Metaparadinitrophenyl metanitrobenzoate is obtained by the action of nitric acid of sp. gr. 1·53 on metanitrophenyl benzoate. It crystallises in bright yellow needles, melts at 149°, and is sparingly soluble in most ordinary solvents, especially in ether and light petroleum. Metanitrophenyl benzoate, when dissolved in a mixture of equal parts of nitric acid of sp. gr. 1·51 and sulphuric acid of sp. gr. 1·82, yields trinitroresorcinol and metanitrobenzoic acid. W. P. W.

Method for the Introduction of Carboxyl into Aromatic Hydrocarbons. By E. Lellmann and O. Bonhöffer (*Ber.*, **19**, 3231).—Benzoic acid can readily be prepared by acting with diphenylcarbamide chloride on benzene in presence of aluminium chloride, and heating the benzoyldiphenylamine so obtained with hydrochloric acid. Paratoluic and xylic acids, [$COOH : Me_2 = 1 : 2 : 4$], were obtained in a similar manner from toluene and metaxylene respectively. Paraxylene does not react with the chloride; hence it would seem that the group $CO{\cdot}NPh_2$ can only take up the para-position with respect to methyl. N. H. M.

Phenylglycidic Acid. By J. Plöchl (*Ber.*, **19**, 3167—3172).—In answer to the communications of Lipp (this vol., p. 142) and E. Erlenmeyer, jun. (*ibid.*), the author upholds the correctness of his view (Abstr., 1884, 604) that his acid $C_9H_8O_3$ is the true phenylglycidic acid, $\overset{O}{\diagup\diagdown}CHPh{\cdot}CH{\cdot}COOH$, and that Glaser's acid is β-hydroxycinnamic acid.

The author finds that paranitrobenzaldehyde forms with hippuric acid a condensation-derivative corresponding with benzoylimidocinnamic anhydride. This substance when heated with fuming nitric acid first forms paranitrobenzoylimidocinnamic acid, but at 120—130° it is

decomposed, yielding a brownish-red compound (a polymeric nitrophenylethylene oxide), whilst carbonic anhydride is at the same time evolved. Lipp's paranitrophenylglycidic acid gives the same decomposition-products. The author points out that in many other cases also the introduction of a nitro-group into the benzene nucleus causes a variation in the behaviour of the side-chain in reactions.

E. Erlenmeyer, jun., objects to the author's formula, because the latter's phenylglycidic acid yields a phenylhydrazine and a hydroxylamine compound and shows the thiophen reaction. The author states that with ammonia his acid gives a compound C_9H_7NO. He believes this compound to have the constitution $CHPh\begin{cases}CH \\ | \\ N-\end{cases}CO$, and thinks that Erlenmeyer's compounds have probably analogous structures.

As further strongly supporting the correctness of his formula, the author cites—(1) the gradual decomposition of the acid, when exposed to moist air, into benzaldehyde and a new acid; (2) the formation of a polymeric phenylethylene oxide (and not Erlenmeyer and Lipp's polymeric phenylethylaldehyde) by the action of hydrochloric acid; and (3) the easy convertibility of the acid into *phenylpyruvic acid;* the latter is easily soluble in boiling water, crystallises in tables, and melts at 160—161°. It is still under investigation.

L. T. T.

Benzoquinonecarboxylic Acids. By J. U. Nef (*Annalen*, **237**, 1—39).—This paper contains a description of the derivatives of durene, durylic acid, and quinonetetracarboxylic acid, which has already been published by the author (Abstr., 1886, 64, 241, 550). The following substances have not been previously mentioned:—The acetic derivative of diamidodurylic acid, prepared by the action of acetic anhydride on the amido-acid at 140°, crystallises in quadratic plates, and melts at 275°.

Dihydroxydurylic acid, $C_6Me_3(OH)_2{\cdot}COOH$ (Abstr., 1886, 241), is soluble in alcohol, ether, and in hot water. The acid forms an amorphous lead salt, and reduces ammoniacal silver nitrate solution. The ethyl salt, $C_6Me_3(OH)_2{\cdot}COOEt$, forms colourless needles. It melts at 109°, and is soluble in hot water, alcohol and the usual solvents, with the exception of light petroleum. The alcoholic solution is oxidised by ferric chloride, *ethyl duroquinonecarboxylate*, $C_6{\cdot}O_2Me_3{\cdot}COOEt$, being formed. This substance is best prepared by the action of an ethereal solution of ethyl iodide on silver duroquinonecarboxylate. It crystallises in golden needles, melts at 51°, and sublimes easily. It is insoluble in cold water, but dissolves freely in alcohol, ether and in (warm) light petroleum. On reduction with sulphurous acid, it yields ethyl dihydroxydurylate. Duroquinonecarboxylic acid is completely converted into *nitropseudocumenequinone*, $C_6O_2Me_3{\cdot}NO_2$, by the action of warm strong nitric acid. The nitroquinone crystallises in golden scales, soluble in ether, chloroform, benzene, light petroleum, alcohol, and nitric acid. It melts at 113°, and sublimes readily. The corresponding *quinol*, $C_6Me_3(OH)_2{\cdot}NO_2$, is obtained by the action of sulphurous acid on the alcoholic solution of the nitroquinone at 100°.

	Properties.	Solutions.	Colour with Fe_2Cl_6.	NaOEt.	Zn + HCl in alcoholic solution.	Oxidation with Br in CS_2.
Ethyl succinosuccinate	colourless needles, m. p. 126—127°	pale blue fluorescence	cherry	colourless, afterwards pale pink	—	ethylic paradihydroxyterephthalate
Ethyl paradiketohexamethylenetetracarboxylate.	colourless needles, m. p. 142—144°	pale blue fluorescence	cherry	colourless, afterwards pale pink	—	ethyl quinoltetracarboxylate
						with HNO_3
Ethyl paradihydroxyphthalate	pale yellow needles or prisms, m. p. 133°	strong blue fluorescence	blue-green	red	ethyl succinosuccinate	*no* quinone
Ethyl quinoltetracarboxylate	yellow needles, m. p. 126—128°	strong blue fluorescence	blue-green	red	ethyl paradiketohexamethylenetetracarboxylate	ethyl quinonetetracarboxylate
Paradihydroxyterephthalic acid	yellow scales	yellowish-green, with green fluorescence	intense blue	—	—	CO_2 evolved: nitranilic acid
Quinoltetracarboxylic acid	pale yellow, broad needles	yellow, with green fluorescence	intense blue	—	—	CO_2 evolved: total decomposition
Ethyl paradiamidoterephthalate....	golden needles, m. p. 168°, strong base	brown, with golden yellow fluorescence	—	—	ethyl succinosuccinate	*no* quinone
Ethyl diamidopyromellitate.....	red prisms, m. p. 134°, feeble base	red, yellowish-red fluorescence	—	—	ethyl paradiketohexamethylenetetracarboxylate	ethyl quinonepyromellitate

It crystallises in golden needles, melts at 106°, and is soluble in ether, alcohol, chloroform, acetic acid and in hot water.

The compound obtained by the reduction of ethyl dinitropyromellitate, and described by the author as ethyl azopyromellitate (Abstr., 1886, 64), is now found to be *ethyl diamidopyromellitate*,

$$C_6(NH_2)_2(COOEt)_4.$$

By reducing the alcoholic solution with zinc-dust and sulphuric acid, ethyl paradiketohexamethylenetetracarboxylate is produced. Ethyl diamidopyromellitate yields a diacetic derivative,

$$C_6(NHAc)_2(COOEt)_4,$$

which crystallises in colourless plates and melts at 149°. It is freely soluble in acetone, chloroform, acetic acid, and hot alcohol. It is not decomposed by boiling with alkalis or with hydrochloric acid.

Ethyl quinoltetracarboxylate, $C_6(OH)_2(COOEt)_4$ (Abstr., 1886, 550), bears a striking resemblance in its properties to Herrmann's ethyl quinonedihydrodicarboxylate, which Baeyer has shown (Abstr., 1886, 445) to be ethyl paradihydroxyterephthalate. *Quinoltetracarboxylic acid* crystallises with $1\frac{1}{2}$ mols. H_2O, which it retains at 100°. It dissolves freely in hot water, forming a fluorescent solution, from which it is precipitated by mineral acids. Ferric chloride gives a blue coloration. The soluble salts of this acid form yellow solutions which exhibit a green fluorescence. Attempts to oxidise quinoltetracarboxylic acid to quinonetetracarboxylic acid were unsuccessful.

Ethyl quinoltetracarboxylate is converted into *ethyl paradiketohexamethylenetetracarboxylate* by shaking the alcoholic solution with zinc-dust and hydrochloric acid (Abstr., 1886, 551). This substance yields ethyl quinoltetracarboxylate on treatment with bromine and carbon bisulphide, and it readily enters into reaction with ammonium acetate and with phenylhydrazine.

The resemblance between the derivatives of ethyl diamidopyromellitate and ethyl succinosuccinate is shown in the table (p. 256).

W. C. W.

Constitution of Azo-opianic Acid. By C. Liebermann (*Ber.*, **19**, 2920—2922).—Although the so-called azo-opianic acid has been recognised as the anhydride of orthamidohemipinic acid, yet hitherto it has not been found possible to convert the latter into the former by the abstraction of the elements of water. In this paper, however, it is shown that both orthamidohemipinic and azo-opianic acids yield an identical acetylazo opianic acid. The last acid, when warmed with alkali and subsequently acidified, yields acetylorthamidohemipinic acid, $C_6H(OMe)_2(COOH)_2{\cdot}NHAc + H_2O$, which crystallises in colourless needles, melting at 160—170° with complete decomposition. The acetyl-group is still retained when the acid is heated with concentrated sulphuric acid; a result to be explained by the former researches of the author and Kleemann, which have proved that the acetyl-group in acetylazo-opianic acid is attached to the nitrogen and not to the oxygen-atom.

V. H. V.

An Isomeride of Hemipinimide. By C. Liebermann (*Ber.*, **19**, 2923—2927).—The author has recently shown that hemipinimide is produced by boiling a mixture of opianic acid with hydroxylamine hydrochloride in equimolecular proportions. If, however, the change be effected at ordinary temperatures, a substance isomeric with hemipinimide is produced, which it is proposed to call *opianoximic anhydride*. It crystallises in long, colourless needles, melting at 114—115°; its alcoholic solution, unlike that of hemipinimide, is not fluorescent. When melted, the substance is converted with considerable development of heat into hemipinimide. This anhydride only displays feeble acidic properties, but on protracted heating with water it is converted into hemipinic acid.

Similarly when ethyl opianate and hydroxylamine hydrochloride are heated, the above anhydride is also formed; all attempts to prepare opianoximic acid have hitherto failed. V. H. V.

Isomeric Aldehydophenoxyacetic Acids. By T. Elkan (*Ber.*, **19**, 3041—3054).—*Paraldehydophenoxyacetic acid*,

$$CHO[1]C_6H_4[4]\cdot OCH_2\cdot COOH\ [CHO : OCH_2 = 1 : 4],$$

is obtained by heating equivalent amounts of parahydroxybenzaldehyde and monochloracetic acid in a silver dish on a water-bath, and adding sufficient caustic soda to give an alkaline reaction. When it begins to solidify, a slight excess of chloracetic acid is added, the solution being always kept alkaline; it is then treated several times with water and evaporated to dryness. The product is dissolved in hot water, precipitated when cold with hydrochloric acid, and the yellowish acid so obtained purified by boiling with calcium carbonate. It crystallises from water in small plates, melting at 198°, is very sparingly soluble in cold water, more soluble in alcohol, ether, benzene, and chloroform, and shows aldehydic properties. It yields a sparingly soluble double compound with hydrogen sodium sulphite, and reduces ammoniacal silver solution, but not Fehling's solution. The *silver salt*, $C_9H_7O_4Ag$, crystallises in needles. Bromine-water acts on the acid with formation of a *bromine-derivative*, $C_9H_7O_4Br$; this crystallises from hot water in slender branched needles, melting at 185°. *Ethyl paraldehydophenoxyacetate* is a crystalline substance which begins to decompose at 100°, and melts at 155°. The *hydroxylamine-derivative*, $C_9H_9O_4N$, forms large spear heads, melting at 145°.

Metaldehydophenoxyacetic acid, $C_9H_8O_4$, is prepared in a manner similar to the para-compound. It crystallises from warm water in slender needles, which melt at 148°, and shows the same aldehydic reaction as the isomeride; it is rather more soluble than the latter. The *silver* and *ethyl salts* were prepared. The *monobromo-derivative* forms lustrous plates, melting at 154°. The *hydroxylamine-compound* crystallises in slender needles, melting at 168°. When oxidised with potassium permanganate, both isomerides yield the corresponding dicarboxylic acids.

Phenoxyacetic-paracarboxylic acid, $COOH[1]\cdot C_6H_4[4]\cdot OCH_2\cdot COOH$ [= 1 : 4], crystallises in white needles, melting at 278°; it dissolves

readily in alcohol, ether and glacial acetic acid, less in benzene and chloroform, and only very sparingly in water. The *silver salt* was analysed. The *phenylhydrazine-derivative*, $C_{15}H_{14}N_2O_3$, forms slender, yellowish-white needles, which melt at 159°, and dissolve sparingly in water, readily in alcohol and ether.

Phenoxyacetic-metacarboxylic acid melts at 206°, and is analogous in its solubility, &c., to the para-acid. The *phenylhydrazine-compound* forms slender needles which melt at about 140°.

Phenoxyacetic-paracrylic acid, $COOH{:}CH{:}CH{\cdot}C_6H_4{\cdot}OCH_2{\cdot}COOH$, is prepared by gently boiling equal parts of paraldehydophenoxyacetic acid and dry sodium acetate with acetic anhydride (3 parts). It melts at 225°, dissolves readily in alcohol, ether, and glacial acetic acid; it is also soluble in benzene and light petroleum.

Phenoxyacetic-metacrylic acid, $C_{11}H_{10}O_5$, is obtained in like manner to the para-compound, and crystallises in needles melting at 219°.

Orthacrylaldehydophenoxyacetic acid,

$$CHO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OCH_2{\cdot}COOH,$$

is prepared by exactly neutralising a dilute solution of orthaldehydophenoxyacetic acid, heating it at 50° to 60°, and gradually adding simultaneously an aqueous solution of acetaldehyde, and 5 per cent. soda solution so as to keep the solution always slightly alkaline. It is then warmed on a water-bath, cooled down, and acidified with dilute sulphuric acid. The acid crystallises from hot water in transparent plates which melt at 153°.

The *meta-acid* crystallises (with 1 mol. H_2O) in long, yellowish needles which melt at 100°.

The *para-acid* forms a crystalline, yellowish precipitate melting at 182°. All three isomerides show aldehydic properties; they combine with hydrogen sodium sulphite, reduce ammoniacal silver solutions, and condense with phenylhydrazine.

Phenoxyacetic-orthacrylic acid methyl ketone,

$$COMe{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}COOH,$$

is obtained by adding pure acetone (from the hydrogen sodium sulphite compound) to the warm slightly alkaline solution of sodium orthaldehydophenoxyacetate. It melts at 108°. The *meta-compound*, $C_{12}H_{12}O_4$, crystallises in well-formed, anhydrous prisms which become opaque when kept. It melts at 122°. The *para-compound* melts at 177—178°.

The *hydroxylamine-derivative* of orthaldehydophenoxyacetic acid (Rössing, Abstr., 1885, 388) crystallises in plates, very readily soluble in hot water, alcohol, and ether, more sparingly in benzene, chloroform, &c. It melts at 138°. N. H. M.

Vanillinoxyacetic Acid. By T. Elkan (*Ber.*, **19**, 3054—3056). —*Vanillinoxyacetic acid*, $CHO{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH$ [= 4 : 2 : 1], is prepared by fusing monochloracetic acid with vanillin in a silver dish, and adding an excess of caustic potash until the solution is distinctly alkaline. After four hours (during which the water lost by

evaporation must be from time to time replaced) the reaction is completed. It crystallises from hot water in slender, yellowish-white needles, melts at 188°, and dissolves readily in ether, alcohol, chloroform, &c. It combines with phenylhydrazine and with hydrogen sodium sulphite, and reduces ammoniacal silver solution. The *copper* and *silver* salts were prepared.

Vanillic-oxyacetic acid, $COOH\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot COOH$ [=4:2:1], is formed in the preparation of vanillinoxyacetic acid, when the treatment with potash and chloracetic acid is too prolonged. It crystallises from water in slender, branched needles which melt at 256°; it dissolves in ether, benzene, chloroform, &c. The *copper salt* has a fine green colour; it is insoluble. N. H. M.

Derivatives of Pyruvic Acid. By G. Gerson (*Ber.*, **19**, 2963—2969). — When ethyl α-cyano-α-hydroxypropionate is treated with phenylhydrazine, a compound melting at 116° and identical with Fischer's ethyl phenylhydrazinepyruvate (Abstr., 1884, 52) is obtained.

Ethyl α-anilido-α-cyanopropionate, $NHPh\cdot CMe(CN).COOEt$, is prepared by treating ethyl α-cyano-α-hydroxypropionate with aniline in alcoholic solution. It crystallises in large, transparent cubes belonging to the rhombic system, with the axial ratio $a:b:c = 0{\cdot}79023:1:1{\cdot}56366$; the following faces were observed: ∞P predominating, ∞P̄∞, ∞P̆∞ narrow, P̄∞ fairly large, P̆∞ smaller than P̄∞. It melts at 101·5°, and is insoluble in water but readily soluble in alcohol and ether.

Ethyl anilidoisosuccinamate, $NHPh\cdot CMe(CONH_2)\cdot COOEt$, is formed when ethyl α-anilido-α-cyanopropionate is dissolved in concentrated sulphuric acid, poured into water, and neutralised with ammonia. It crystallises from benzene in slender, white needles, melts at 86°, is sparingly soluble in cold water, readily soluble in hydrochloric acid, alcohol and benzene, but insoluble in light petroleum. The crystalline *hydrochloride* is very soluble in water. On boiling ethyl anilidoisosuccinamate with a solution of soda as long as ammonia is evolved, acidifying with acetic acid, converting into lead salt, and decomposing it with hydrogen sulphide, *α-anilidopropionic acid*, $NHPh\cdot CMeH\cdot COOH$ (Tiemann and Stephan, Abstr., 1883, 199), is obtained in white crystals melting at 160°.

Ethyl α-orthotoluido-α-cyanopropionate, $C_7H_7\cdot NH\cdot CMe(CN)\cdot COOEt$, prepared in a similar manner to the anilido-compound, crystallises in rosettes of small, white needles, melts at 93°, and is insoluble in water, sparingly soluble in cold alcohol, readily soluble in hot alcohol and benzene. On treating it with concentrated sulphuric acid, and neutralising with ammonia, it yields *ethyl orthotoluidoisosuccinamate*,

$$C_7H_7\cdot NH\cdot CMe(CONH_2)\cdot COOEt,$$

which crystallises in long, transparent needles, and resembles the anilido-compound in all its properties. By boiling the isosuccinamate with potash solution, &c., *orthotoluidopropionic acid*,

$$C_7H_7\cdot NH\cdot CMeH\cdot COOH,$$

is obtained in slender, white needles which melt at 116°, and dissolve readily in water, alcohol, and benzene.

Ethyl α-paratoluido-α-cyanopropionate crystallises in light brown, glistening spangles, melts at 80·5°, and is insoluble in alcohol and benzene, sparingly soluble in water.

Ethyl αα-naphthylamido-α-cyanopropionate forms slender, white scales which melt at 134°, and are readily soluble in alcohol and benzene, sparingly soluble in cold water. By treatment with sulphuric acid, &c., *ethyl α-naphthylamidoisosuccinamate* is obtained in long white needles melting at 159°. It dissolves readily in alcohol and benzene, sparingly in cold water.

Ethyl αβ-naphthylamido-α-cyanopropionate crystallises in small rosettes, is almost insoluble in water and cold alcohol, soluble in hot alcohol and benzene, and decomposes at 200° without melting.

W. P. W.

Two New Diketonic Acids. By W. Kues and C. Paal (*Ber.*, **19**, 3144—3148).—The authors have examined the insoluble crystalline substance obtained by them during the hydrolysis of ethyl benzoylisosuccinate (Abstr., 1886, 354), and find it to be *ethyl diphenacylmalonate*, $C(CHBz)_2(COOEt)_2$. Its formation must be due to the formation of some ethyl disodiomalonate and the action of the bromacetophenone thereon. This substance forms large, colourless prisms, melts at 118—119°, and distils almost without decomposition. It is easily soluble in water, benzene, acetic acid, and carbon bisulphide, more sparingly in alcohol, and is insoluble in light petroleum. It reacts strongly with phenylhydrazine, but no homogeneous substance could be isolated from the product. Hydroxylamine is without action on it, as are also aqueous solutions of the alkalis. When digested with strong alcoholic potash, it is saponified, and yields *diphenacylmalonic acid*, crystallising in colourless prisms, melting with evolution of carbonic anhydride at 134°. It is sparingly soluble in water, easily so in ether, alcohol and acetic acid, insoluble in benzene. It forms a compound with phenylhydrazine. When carefully melted, carbonic anhydride is evolved and *diphenacylacetic acid*, $CH(CH_2Bz)_2{\cdot}COOH$, is formed. This crystallises in silky needles, easily soluble in ether, alcohol, and benzene, and melts at 132—133°. When heated with an acetic solution of phenylhydrazine, it yields a compound of the formula $C_{30}H_{26}N_4O$, crystallising in white needles which melt at 164—166°, and are soluble in alcohol and acetic acid, insoluble in alkalis. The hydrazine-compound is not decomposed by dilute acids. Adopting the views of the composition of such compounds advocated by E. Fischer and W. Roser, the authors consider the following as the most probable formula for this substance:—

$$N_2HPh:CPh{\cdot}CH_2{\cdot}CH<\begin{matrix}CO{\cdot}NPh-\\CH_2{\cdot}CPh\end{matrix}>N.$$

L. T. T.

Action of Zinc Alkyl Compounds on Ethyl Malonate. By E. Lang (*Ber.*, **19**, 2937—2939).—Zinc methyl or zinc ethyl acts at ordinary temperatures on ethyl malonate with evolution of methane and ethane, and formation of a crystalline magma of ethyl phloro-

glucinoltricarboxylate, $C_6(OH)_3(COOEt)_3$. The reaction thus consists of the abstraction of the elements of alcohol and subsequent condensation. V. H. V.

Furfurane-derivatives from Resorcinol. By A. Hantzsch (*Ber.*, **19**, 2927—2934).—It has been shown that the sodium compounds of the monohydric phenols, when treated with ethyl chloracetate, yield at first ethyl phenoxyacetoacetate, and finally ethyl furfurocarboxylate. The dihydric phenols undergo a similar but more complicated reaction, according as the mono- or di-sodium compound reacts with one or two molecules of the ethereal salt. In the former case, hydroxycumarones are obtained, in the latter, benzodifurfuro-derivatives, the nature of the isomerism of which is dependent on the relative position of the carbon-atom to which the furfuryl-ring is attached. Thus in the case of resorcinol two such isomeric hydroxy- and difurfuro-derivatives are possible, precisely as two quinolines, the meta- and the ana-series, are synthetically formed from amines of the meta-series.

Ethyl metahydroxycumarilate, $OH{\cdot}C_8OH_3{\cdot}COOEt$ [OH : COOEt : Me = 2 : 2′ : 3′], formed from mono-sodium resorcinol and ethyl chloracetate, crystallises in white needles melting at 178°, readily soluble in ether. The corresponding acid crystallises with $\frac{1}{2}$ mol. H_2O in needles which melt at 226°, with evolution of carbonic anhydride and formation of *hydroxymethylcumarone*, $C_8OH_4Me{\cdot}OH$. This compound crystallises in needles melting at 96—97°, soluble in water, alcohol, and ether.

From disodium resorcinol and ethyl chloracetate, two isomeric ethyl benzodimethylfurfurodicarboxylates are formed, the nature of the isomerism of which is analogous to that of anthracene and phenanthrene. These are provisionally designated the α- and β-series, as the experimental results are insufficient to fix the formula of each compound.

Ethyl metabenzodimethyl-α-difurfurocarboxylate, $C_{10}O_2H_2Me_2(COOEt)_2$, crystallises in needles melting at 186°, and its isomeride in more soluble aggregates, melting at 140—141°. Both isomeric ethereal salts are readily saponified; the corresponding acids melt above 310° with decomposition, and are sparingly soluble in water, but more soluble in alcohol. Both the acids and their salts are difficult to distinguish one from the other. Only one of the isomeric difurfuranes, $CH<\overset{CMe}{\underset{O}{\rangle}}C_6H_2<\overset{CMe}{\underset{O}{\rangle}}CH$, is described, corresponding with the ethereal salt which melts at 186°; it is a clear brown oil, boiling at 270°, solidifying in a freezing mixture, and melting at 17°; with concentrated sulphuric acid, it gives a light blue coloration resembling that obtained with cœruglignone. V. H. V.

Furfurane-derivatives from Phloroglucinol. By E. Lang (*Ber.*, **19**, 2934—2937).—The reactions between the butyric alcohol, phloroglucinol, and ethyl chloracetate in presence of sodium ethylate, are analogous to those of resorcinol described in the preceding Abstract. The three series of compounds are formed in a similar way, yet the presence of alcohol is necessary for the production of

the dihydroxy-product, and its absence for that of the trifurfuraldehyde-derivatives.

Ethyl meta-α-dihydroxymethylcumarilate, $C_8OH_2Me(OH)_2{\cdot}COOEt$, forms small white needles melting at 242°, readily saponified and converted into the corresponding acid, which crystallises with ½ mol. H_2O, and melts at 281° with evolution of carbonic anhydride.

Ethyl benzotrimethyltrifurfurocarboxylate, $C_6(<_{-O-}^{CMe}>C{\cdot}COOEt)_3$, obtained by treating trisodium phloroglucinol with 3 mols. of ethyl chloracetate, crystallises in satiny needles, melting at 296—298°, sparingly soluble in all menstrua. The corresponding acid separates with 1 mol. H_2O in a gelatinous form. On distillation with alkali, the benzotrimethyltrifurfurane, $C_6(<_{-O-}^{CMe}>CH)_3$, is obtained; it crystallises in needles melting at 115—120°, and is very soluble in most menstrua. V. H. V.

Sulphobenzidedisulphonic Acid. By R. Otto and A. Rössing (*Ber.*, **19**, 3124—3129).—*Sulphobenzidedisulphonic acid*,

$$SO_2 : C_{12}H_8(SO_3H)_2,$$

is prepared as already described (Abstr., 1879, 649), by the action of sulphuric hydroxychloride (2 mols.) on sulphobenzide. It is very probably the dimetasulphonic acid. It forms a yellowish, fibro-crystalline, deliquescent mass, readily soluble in alcohol and water, but insoluble in ether and benzene. It forms only normal salts. The potassium salt crystallises with 1 mol. H_2O; the sodium with 3 mols. H_2O, calcium with 6½ mols. H_2O, barium 5 mols. H_2O, copper with 3½ mols. H_2O, and the lead salt with 3 mols. H_2O. The *chloride* crystallises in small, fatty plates, and melts at 175—176°. The *amide* forms white needles, melts at 240°, is nearly insoluble in ether and benzene, sparingly soluble in boiling water, more soluble in alcohol. The *anilide* forms lustrous, white plates, and melts at 212°. The *ethyl* salt melts at 81—82°. The *diphenylsulphone*, $SO_2(C_6H_4{\cdot}SO_2Ph)_2$, is obtained in small quantity by heating the disulphonic acid with benzene and phosphoric anhydride; it melts at 192—193°.

Experiments to obtain a trisulphonic acid from sulphobenzide were unsuccessful. A. J. G.

Non-existence of Claesson's Phenylsulphineacetic Acid. By R. Otto and E. Engelhardt (*Ber.*, **19**, 3138—3141).—Claesson states (this Journal, 1876, i, 567) that he obtained the above acid (aceto-phenylsulphinic acid), $Ph{\cdot}SO{\cdot}CH_2{\cdot}COOH$, by the partial oxidation of phenylthioglycollic (phenylthiacetic) acid. The authors have carefully repeated these experiments, and find that the substance described by Claesson was not a homogeneous compound, but a mixture of phenylsulphonacetic acid, $Ph{\cdot}SO_2{\cdot}CH_2{\cdot}COOH$, with unoxidised phenylthioglycollic acid. L. T. T.

Metatoluenesulphonic Acid and its Salts. By K. Vallin (*Ber.*, **19**, 2952—2953).—The metatoluenesulphonic acid employed in the previous research (Abstr., 1880, 256) contained para-acid as an

impurity; the author has, therefore, repeated the work with pure meta-acid obtained from toluidinesulphonic acid [CH_3 ; SO_3H : NH_2 = 1 : 3 : 4] by diazotising and boiling with alcohol. The acid crystallises in slender needles or thin scales. The potassium, sodium, silver, calcium, barium, lead, magnesium, zinc, cadmium, and copper salts are described. The *chloride*, $C_7H_7{\cdot}SO_2Cl$, has not been solidified; the *amide* crystallises from water in laminæ melting at 107°, from alcohol in monoclinic crystals melting at 108°. At 14°, 1 part of the amide dissolves in 376·7 parts of water and 5·74 parts of alcohol. The *hydrosulphide*, $C_7H_7{\cdot}SH$, boils at 195—205°, and does not solidify at −20°.

Sodium paratoluenesulphonate does not crystallise with 3 mols. of H_2O, but either with 2 mols. in laminated masses, or at low temperatures in rectangular tables with probably 4 mols. H_2O. The hydrosulphide of the para-acid melts at 43—44° and boils at 194°, that of the ortho-acid melts at 15° and boils at 193°. W. P. W.

Toluenedisulphonic Acids. By P. Klason (*Ber.* **19**, 2887—2890).—Toluenemetasulphonic acid is convertible into a mixture of two disulphonic acids, separable by the difference in solubility of their barium salts, the less soluble separating with 1 mol. H_2O as a crystalline powder. Its potassium salt crystallises with 1 mol. H_2O in pointed prisms, the acid chloride in rhombic tables melting at 96°, and the amide in minute prisms melting at 224°. This acid is identical with one obtained by Håkausson from the mother-liquors of potassium α-toluenedisulphonate. The more soluble barium salt crystallises in prisms containing $3\frac{1}{2}$ mols. H_2O, the chloride in truncated prisms melting at 95°; the amide melts at 214°. This acid is identical with one obtained by Limpricht from toluidinedisulphonic acid. V. H. V.

Cumene-orthosulphonic Acid and Orthocumic Acid. By A. Claus and J. A. Schulte im Hof (*Ber.*, **19**, 3012—3017).—When cumene-β-sulphonic acid (Abstr., 1885, 903) is oxidised with chromic mixture, it is destroyed without formation of intermediate products; it is therefore concluded that the acid has the constitution [C_3H_7 : SO_3H = 1 : 2].

Orthocumic acid, $CHMe_2{\cdot}C_6H_4{\cdot}COOH$, is obtained by fusing the potassium or barium salt of the above sulphonic acid with sodium formate; it is insoluble in cold water, readily soluble in alcohol, ether, glacial acetic acid, &c. When heated at 200°, it becomes brown and partly sublimes and does not melt at 300°. It distils with steam. The *barium* and *calcium salts* (each with 2 mols. H_2O) and the *magnesium salt* (with 6 mols. H_2O) crystallise in needles readily soluble in water. The alkali salts are crystalline but very hygroscopic. The *chloride* forms a yellow oil readily soluble in ether, chloroform, &c.; when treated with dry ammonia, it is converted into the *amide*. The latter crystallises from alcohol in small needles melting at 124° (uncorr.).

Orthocumic acid is not acted on by chromic mixture of ordinary strength. When oxidised with potassium permanganate, it is con-

verted into phthalic acid; no hydroxycumic acid is formed. The reaction is of interest, as showing that the reaction by which isopropyl in paracumic acid is oxidised to hydroxyisopropyl does not hold good when the isopropyl-group is in the ortho-position to carboxyl (R. Meyer, Abstr., 1878, 878). N. H. M.

Action of Aldehydes, Anhydrides, and Diazo-compounds on the three Methylindoles. By E. Fischer (*Ber.*, **19**, 2988—2991). —When benzaldehyde (1 part) is heated with methylketole (2 parts) at 100°, an almost quantitative yield of *benzylidenemethylketole*, $Ph{\cdot}CH : (C_9H_8N)_2$, is obtained. This substance crystallises well from acetone, and most probably has the constitution

$$NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C{\cdot}CHPh{\cdot}C<\begin{matrix}C_6H_4\\CMe\end{matrix}>NH.$$

With paraldehyde and zinc chloride, methylketole yields a crystalline compound soluble in hot alcohol and in acetone. 1′ Methylindole combines slowly with benzaldehyde at 100°, the reaction, however, is hastened by the addition of a small quantity of zinc chloride; the product crystallised from acetone melts at 197°, and is isomeric with that obtained from methylketole. Skatole and benzaldehyde on the contrary combine only slowly in the presence of zinc chloride at 100°, and the resulting compound, which forms colourless crystals, differs from the preceding derivatives in its much greater solubility and lower melting point.

Equal parts of phthalic anhydride and methylketole heated at 100° with zinc chloride yield a compound, $C_9H_9N{\cdot}C_8H_4O_3$, which when heated to about 200° is converted into an acid, $C_9H_8N{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, with loss of carbonic anhydride. From 1′ methylindole at 100° a compound having different properties is obtained. The action of acetic anhydride on methylketole in the presence of sodium acetate has already been studied (Abstr., 1881, 734); since, however, the acetyl derivative reacts with phenylhydrazine to form a compound, $C_{17}H_{17}N_3$, and is therefore a ketone, Jackson's formula, $C_6H_4<\begin{matrix}CH\\NAc\end{matrix}>CMe$, must be regarded as incorrect; the substitution of acetyl occurring probably in the position 3′. When 1′ methylindole is heated at 100° with acetic anhydride and zinc chloride, a ketone is obtained which is probably identical with Baeyer's acetylindole (Abstr., 1879, 938). Methylketole readily reacts with diazobenzene chloride in the presence of acetates dissolved in weak alcohol, and forms an azo-compound of the composition $C_6H_5{\cdot}N : N{\cdot}C_9H_8N$. It crystallises in yellow needles, melts at 115—116°, and by reduction with zinc and hydrochloric acid yields aniline and amidomethylketole. W. P. W.

Hydrocarrotene and Carrotene. By F. Reinitzer (*Monatsh. Chem.*, **7**, 597—608).—Two crystalline substances have been extracted from carrots, the one, colourless, hydrocarrotene, the other, dark red, carrotene; these have been more recently examined by Huseman and Arnaud, the latter of whom has found carrotene associated with chlorophyll in the leaves of various plants, and assigns to it the formula

of an unsaturated hydrocarbon, $C_{26}H_{38}$, whilst hydrocarrotene is considered to be allied to cholesterin.

The method used for the extraction of these substances is fully described, as also their separation from one another by frequent recrystallisation from boiling acetone and methyl alcohol. Hydrocarrotene is insoluble in water, sparingly soluble in cold, more readily in boiling alcohol, very soluble in acetone, from which it crystallises out in long needles, but from methyl alcohol in micaceous leaflets. It contains 5 per cent. of water, melts at 137·4°; $[\alpha]_D = -37·4°$, $t = 21°$, $C = 4·131$ in chloroform. In these physical properties, as also in various chemical reactions, it resembles cholesterin, a view further confirmed by the formation of its acetate and benzoate, the melting points and specific rotatory powers of which are compared with those of other cholesterins. Hydrocarrotene appears to be more nearly identical with phytosterin, although it is thought advisable for the present to retain its particular name. From cholesterin itself, hydrocarrotene differs in its behaviour with bromine, which is at first absorbed, and subsequently the change is accompanied with evolution of hydrobromic acid. The bromide formed crystallises in long, colourless, transparent needles, moderately soluble in alcohol, readily soluble in ether and carbon bisulphide. Husemann's observation that hydrocarrotene is converted into carrotene by bromine is apparently erroneous. The improbability that carrotene, a coloured substance, is a hydrocarbon, is pointed out, although no experiments are described, but allusion is made to the similarity of carrotene to a colouring matter present in the paradise apple, *Lycopersicum esculentum*.

V. H. V.

Diphenylmetaxylylmethane and Diphenylorthoxylylmethane. By W. Hemilian (*Ber.*, **19**, 3061—3075).—*Diphenylmetaxylylmethane*, $CHPh_2·C_6H_3Me_2$ [Me : Me : $CHPh_2 = 1 : 3 : 6$], is prepared in a manner similar to diphenylparaxylylmethane (Hemilian, Abstr., 1884, 321) by heating benzhydrol, dissolved in pure metaxylene, with phosphoric anhydride for four hours at its boiling point. The product is treated with water and with aqueous soda, and the oil distilled. It solidifies when kept for a few days, and is purified by treating a warm, saturated solution in glacial acetic acid with twice the amount of ether, and allowing it to evaporate slowly. It forms large six-sided prisms which melt at 61·5° and distil above 360°. It dissolves readily in alcohol, ether, benzene, &c. When boiled for a long time with chromic mixture, and the product extracted with boiling soda solution, an insoluble residue is obtained, consisting of *diphenylmethylphthalide*, $CPh_2<^{C_6H_3Me}_{O·CO}>$; this crystallises from alcohol in lustrous prisms, which melt at 147° and distil at above 360° without change; it is soluble in ether, benzene, &c., insoluble in aqueous alkalis.

Methyltriphenylmethanecarboxylic acid, $CHPh_2·C_6H_3Me·COOH$, is obtained by boiling diphenylmethylphthalide with alcoholic soda solution, and reducing the sodium salt of the hydroxy-acid so formed by boiling with zinc in alkaline solution. It forms large, lustrous tabular crystals, which melt at 203° and distil without change. It is

rather readily soluble in hot alcohol, ether and acetic acid. The *barium salt* (with 3 mols. H_2O) crystallises in slender needles, almost insoluble in water, rather readily soluble in boiling 70 per cent. alcohol. Other salts were prepared. When carefully oxidised, it is reconverted into diphenylmethylphthalide. When the solution of the acid in strong sulphuric acid is poured into water, a precipitate is obtained consisting of *methylphenylanthranol*, $C_{21}H_{16}O$. It crystallises from alcohol in small yellow plates which soften at 150° and melt at 170°; when oxidised, it is converted into *methylphenylhydroxanthranol*, $C_6H_3Me<^{CPh(OH)}_{-CO\cdot C_6H_4-}>$. The latter forms large colourless prisms melting at 213°; it is insoluble in aqueous alkali; the solution in sulphuric acid has an intense purple-red colour. When distilled with an excess of alkali, paramethyltriphenylmethane is obtained identical with that prepared by E. and O. Fischer from phenylparatolylcarbinol and benzene (Abstr., 1879, 384).

Diphenylphthalidecarboxylic acid, $O<^{CPh_2}_{-CO-}>C_6H_3\cdot COOH$, is contained, as sodium salt, in the alkaline extract from the oxidation experiment with diphenylmetaxylylmethane. It crystallises from warm alcohol in large, tabular crystals (with 1 mol. EtOH); it is insoluble in water, readily soluble in alcohol, ether, benzene, &c.; it melts at 228° and distils unchanged. The *calcium salt* (with 3 mols. H_2O) crystallises from 70 per cent. alcohol in slender, lustrous needles; the *silver salt* crystallises from the same solvent in hair-like needles, insoluble in water. When the acid is distilled with excess of baryta, benzophenone and barium isophthalate are formed.

Triphenylmethanedicarboxylic acid, $CHPh_2\cdot C_6H_3(COOH)_2$[=1:2:4] is prepared by the action of zinc-dust on the alcoholic solution of the anhydro-acid. It forms slender, lustrous needles, readily soluble in alcohol and acetic acid. It melts at 278°, and partly sublimes at a higher temperature. The *calcium salt* (with 2 mols. H_2O) forms matted, microscopic needles; the *barium* and *silver salts* are also described. When distilled with excess of baryta, it is converted into triphenylmethane.

Diphenylortho-xylylmethane, $C_6H_3Me_2\cdot CHPh_2$ [1 : 2 : 5], was prepared from ortho-xylene (from orthobromotoluene). It crystallises in long, lustrous needles, melts at 68·5° and distils at above 360°. It is readily soluble in alcohol, ether, benzene, &c. When oxidised with chromic mixture, a mixture of acids is obtained, but no indifferent phthalide-derivative. When the mixed acids are treated with potassium permanganate, *triphenylcarbinol-dicarboxylic acid*,

$$OH\cdot CPh_2\cdot C_6H_3(COOH)_2,$$

is formed. The latter forms silky, matted, slender needles, very readily soluble in alcohol, ether, and glacial acetic acid, rather soluble in boiling water, and sparingly soluble in benzene. The *salts*, with the exception of the alkali salts, are very sparingly soluble. The acid melts at 180° with effervescence, and is converted into the *anhydride*, $C_{21}H_{14}O_4$. This is a transparent, amorphous substance, readily soluble in alcohol, ether, and benzene. Boiling water has no action on it. When the acid is distilled with an excess of baryta, it is converted into triphenylcarbinol. N. H. M.

Diamidostilbene and Diamidostilbenesulphonic Acid. By F. Bender and G. Schultz (*Ber.*, **19**, 3234—3239).—By reducing orthonitrotolueneparasulphonic acid, Neale obtained an azosulphonic acid, which, when treated with stannous chloride, yielded a compound which he described as hydrazotoluenesulphonic acid (Abstr., 1880, 806). The authors show that this compound is toluidinedisulphonic acid, as it yields toluidine when distilled with lime.

Diamidostilbenesulphonic acid,

$NH_2 \cdot C_6H_3(SO_3H) \cdot CH : CH \cdot C_6H_3(SO_3H) \cdot NH_2$ [$SO_3H : NH_2 = 2 : 4$],

is obtained by dissolving 50 grams of sodium paranitrotolueneorthosulphonate in boiling water, gradually adding 100 c.c. of 33 per cent. soda solution. The solution is diluted, 50 grams of zinc-dust are then gradually added, and the whole boiled until the colourless solution no longer becomes coloured on exposure to air. It is filtered, precipitated with hydrochloric acid, again filtered, and dried. It is almost insoluble in water. The salts are readily soluble. When distilled with soda-lime, it yields stilbene. The base obtained by Klinger by the action of zinc chloride on the condensation product from paranitrotoluene and sodium methoxide (*Ber.*, **16**, 943), and described by him as diamidobenzyltoluene, is shown by the authors to be diparamidostilbene; the same base was also prepared by the reduction of dinitrostilbene from paranitrobenzyl chloride. The properties of the base are as described by Klinger (*loc. cit.*), except that the acetyl-derivative melts at 312° (not 212°).

By combining tetrazostilbene chloride with 2 mols. of α-naphtholsulphonic acid, a blue-violet dye is formed. With β-naphtholdisulphonic acid (R), α-naphthylaminesulphonic acid and salicylic acid (each 2 mols.), blue, red, and yellow azo-dyes are formed respectively. N. H. M.

Brominated Derivatives of Diphenic Acid. By A. Claus and M. Erler (*Ber.*, **19**, 3149—3156).—Bromine, even in the nascent state, acts exceedingly slowly at ordinary atmospheric temperature on diphenic acid, but at 60° and upwards reaction takes place readily. If less than 2 mols. of bromine are employed to 1 mol. acid, a part of the acid remains unacted on. At temperatures from 60—120°, the product consists of a mixture of bromodiphenic acid and bromodiphenic acid dibromide; at temperatures ranging from 120—200°, part of the latter derivative is converted into dibromodiphenic acid, and above 200° only mono- and di-bromodiphenic acids are found in the product of bromination.

Bromodiphenic acid, $COOH \cdot C_6H_4 \cdot C_6H_3Br \cdot COOH$, crystallises in acicular prisms melting at 235—236° (uncorr.). It is not volatile in steam, and sublimes only with considerable decomposition, the small sublimate (melting slightly lower than the acid) appearing to be the *anhydride*. The acid is very sparingly soluble in boiling water, easily in alcohol, ether, and benzene. The neutral and acid *sodium salts* are very soluble, the *barium* (with $3H_2O$), *silver*, and *copper* neutral salts are very sparingly soluble in water. The *ethyl salt* forms crystals melting at 65° (uncorr.). *Bromodiphenic acid dibromide* is

always formed (sometimes to the extent of 15 per cent.) in the bromination below 200° of diphenic acid, but its production from the bromo-acid already formed appears only to take place to a very slight extent. It is sparingly soluble in alcohol and cold chloroform, and crystallises in colourless glistening needles having a very bitter taste. It turns brown at 200°, and melts at about 256° (uncorr.) with decomposition. Heated in closed tubes at 200°, it undergoes decomposition, dibromodiphenic acid being formed. The dibromide is very sparingly soluble in the usual solvents, but dissolves readily in alkalis and alkaline carbonates, to form solutions of unstable salts, which, especially when warmed, rapidly decompose into salts of dibromodiphenic acid. It is soluble in concentrated sulphuric acid and in fuming nitric acid, and is reprecipitated unchanged on the addition of water. The neutral *sodium* salt forms glistening scales, but its solution is rapidly decomposed if boiled.

Dibromodiphenic acid, $C_{12}H_6Br_2(COOH)_2$, is easily soluble in alcohol, ether, and glacial acetic acid. It crystallises in needles, melts at 245° (uncorr.), and is not volatile in steam. It sublimes with difficulty, yielding the *anhydride*. Its *alkali* salts are easily soluble, the *calcium* (with $3H_2O$), *silver*, and *lead* salts sparingly soluble. The *ethyl* salt is crystalline, and melts at 105—106°. This dibromodiphenic acid is evidently isomeric, but not identical, with that (melting at 295° obtained by Ostermayer, *Ber.*, **7**, 1091) from dibromophenanthraquinone.

When the bromo-acids are subjected to dry distillation with lime, brominated diphenylene ketones are formed. *Bromodiphenylene ketone*, $C_{12}H_7Br:CO$, forms yellow scales melting at 122° (uncorr.), and is easily soluble in alcohol, ether, benzene, &c., very sparingly in water. When heated with zinc-dust, it yields fluorene. No hydrogen sodium sulphite compound could be obtained. *Dibromodiphenylene ketone* forms yellow scales melting at 133° (uncorr.). L. T. T.

β-Naphthol-β-Disulphonic Acid. By A. Claus and O. Schmidt (*Ber.*, **19**, 3172—3179).—The authors have endeavoured to determine the constitution of this acid by the action of phosphoric chloride on it. The material used was the commercial sodium salt (the so-called G-salt). Reaction takes place readily, but if only the temperature of the water-bath is used, *β-naphtholdisulphonic chloride* is produced. This is a thick, reddish-brown liquid, and neither it nor the corresponding amide could be obtained in a crystalline form.

If the sodium salt is heated at 100—200° with more than two molecular proportions of the pentachloride, the principal products are ethereal phosphates corresponding with those obtained by Claus and Zimmermann from β-naphtholsulphonic acid (Abstr., 1881, 914).

If the reaction is carried out above 200° (under pressure), and with a large excess (5 mols.) of the pentachloride, dichloronaphthol and trichloronaphthalene are formed. The yield is, however, small, 100 grams of salt only yielding about 6 to 8 grams of chloro-derivatives. Dichloronaphthalene (probably from impurity of monosulphonate in the salt) and tetrachloronaphthalene are also always present in small

quantity. The *dichloronaphthol* is easily isolated, as it alone of the products is soluble in alkalis. It crystallises in colourless needles, which melt at 125° (uncorr.), and sublime with partial decomposition. It is moderately soluble in boiling water, easily in alcohol, ether, &c. The *trichloronaphthalene* is readily soluble in ether, benzene, chloroform, glacial acetic acid and boiling alcohol. It crystallises in white needles, melts at 90° (uncorr.), and may be sublimed. It is not identical with the trichloronaphthalene of the same melting point obtained by Claus and Knyrim (Abstr., 1886, 156). When heated with dilute nitric acid at 210°, it yields a *dichlorophthalic acid*, a yellow syrup, which could not be obtained in a crystalline form. The *potassium*, *sodium*, and *barium* salts are easily soluble, the *silver* salt sparingly soluble, the *lead* salt insoluble. This acid is being further investigated. When heated with chromic acid in acetic solution, the trichloronaphthalene yields a *trichloronaphthaquinone*, which, however, is very readily further oxidised to a chlorinated phthalic acid. Attempts to separate the quinone from the unchanged trichloronaphthalene were unsuccessful, but alkalis removed it in form of a salt of a chlorinated hydroxyquinone. The best result was, however, obtained by treating the mixture with aniline, when *dichloronaphthaquinone anilide*, $C_{10}H_3Cl_2O_2{\cdot}NHPh$, was obtained. This is almost insoluble in water, sparingly soluble in ether. It crystallises in dark reddish-violet scales, melts at 228°, and may be sublimed. The formation of this anilide by the displacement of a chlorine-atom (the corresponding quantity of hydrochloric acid being formed) leaves no doubt that the original quinone is a trichlorinated compound. But as experience teaches that if in a chlorinated naphthalene a chlorine-atom is present in the α-position, that chlorine-atom is expelled in the formation of an α-naphthaquinone, the above trichloronaphthalene must have the constitution $[Cl_3 = 2 : 3 : 2']$. Which of the chlorine-atoms represents the hydroxyl, and which the sulphonic groups in the original acid cannot yet be decided.

L. T. T.

Action of Aldehydes on Phenols. By L. Claisen (*Ber.*, **19**, 3316—3320).—When α-naphthol is treated with benzaldehyde, a white pulverulent compound, *benzaldi-α-naphthol*, $CHPh(C_{10}H_6{\cdot}OH)_2$, is obtained, which turns brown on exposure to the air and dissolves readily in alkalis, the alkaline solution assuming a dark reddish-violet but unstable colour when oxidised.

The reaction, however, proceeds differently when β-naphthol is treated with benzaldehyde. When an acetic acid solution of the two, to which a few drops of hydrochloric acid has been added, is maintained at a low temperature, *benzalglycoldinaphthylacetal*,

$$CHPh(OC_{10}H_7)_2,$$

separates as a crystalline compound melting at 203—205°, and sparingly soluble in ordinary solvents, almost insoluble in aqueous alkalis. Heated with acetic acid and a few drops of hydrochloric acid at 100°, it is converted into *benzaldi-naphthyl oxide*,

$$C_7H_6{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}O,$$

this melts at 189—190°, crystallises well, and is insoluble in alkalis. Benzaldi-naphthyl oxide is also obtained when the acetic acid solution of benzaldehyde and β-naphthol with a little hydrochloric acid or sulphuric acid, is heated at 100°, or in the absence of the acids at 200°.

The author has also obtained results which are not in complete accordance with those published by Claus and Trainer (this vol., p. 231), and points out that the ethylidenediphenol described by them has already been prepared by Fabinyi (*Ber.*, **11**, 283). With acetaldehyde, β-naphthol yields compounds similar to those formed when it is treated with benzaldehyde; thus either *ethylidenedinaphthylacetal*, $C_2H_4(OC_{10}H_7)_2$, melting at 200—201°, or *ethylidene-β-dinaphthyl oxide*, $C_2H_4 : (C_{10}H_6)_2 : O$, melting at 173°, is obtained; both crystallise well and are insoluble in alkalis. The compound described as dinaphthylacetal by Claus and Trainer, but melting at 162–163°, was not obtained in the author's experiments.

The remainder of the paper is devoted to a theoretical discussion, in which the author states his views as to the cause of the difference in behaviour of α- and β-naphthol under these conditions, and arrives at conclusions at variance with those put forward by Claus and Trainer (*loc. cit.*). W. P. W.

α-Naphthyl Methyl Ketone. By A. Claus and P. Feist (*Ber.*, **19**, 3180—3182).—The authors have also independently obtained this ketone lately described by Pampel and Schmidt (this vol., p. 252), but some of their results differ from those of the latter authors. They find that the ketone solidifies if cooled below 0°, and the crystals then melt at 34°. They find the melting point of the acetoxime to be 145° (uncorr.), that of the hydrazine 173° (uncorr.).

When this ketone is treated in the cold with a dilute aqueous solution of the theoretical quantity of potassium permanganate, *α-naphthylglyoxylic* (*α-naphthoylformic*) *acid*, $C_{10}H_7{}^{\alpha}\cdot CO\cdot COOH$, is formed. This acid is a thick oil which only solidifies slowly and with difficulty. It is very unstable, and is easily oxidised by dilute nitric acid or warm permanganate to α-naphthoic acid and carbonic anhydride. The *calcium* and *barium* salts (each with $4\frac{1}{2}H_2O$) are easily, the *silver* salt very sparingly, soluble. The formation of α-naphthoic acid proves this acid to be an α-naphthyl-derivative. It is probably identical with Bössneck's acid melting at 113·5° (Abstr., 1883, 808); the difficulty experienced in crystallising it being in all probability due to traces of oily impurity. L. T. T.

Pyrene. By E. Bamberger and M. Philip (*Ber.*, **19**, 3036—3040). — *Naphthalenetetracarboxylic dianhydride*, $C_{14}H_4O_6$, is obtained by slowly heating naphthalenetetracarboxylic acid (Abstr., 1886, 948) to 150—170°, or by recrystallising the acid from glacial acetic acid. It does not change when heated at 300°, at a higher temperature it sublimes in lustrous needles an inch long. When naphthalenetetracarboxylic acid is suddenly heated to 200—250°, it is converted partly into the anhydride and partly into naphthalenetricarboxylic acid.

Naphthalenetetracarboxylic diimide, $C_{14}H_6O_4N_2$, is formed when the anhydride is treated with aqueous ammonia, and separates in groups of branched needles. It is very sparingly soluble, does not alter in appearance at 270°, and sublimes at a higher temperature in yellow, lustrous needles. The formation of the above dianhydride and diimide shows that the two pairs of carboxyl-groups in naphthalenetetracarboxylic acid have the ortho-position.

Pyrene ketone, $C_{15}H_8O$, crystallises from alcohol in gold-coloured lustrous plates melting at 142°; when oxidised with potassium permanganate, it is converted into Behr and Van Dorp's naphthalic acid (*Annalen*, **172**, 266). N. H. M.

Terebenthene-derivatives. By Pesci and Bettelli (*Arch. Pharm.* [3], **24**, 1037).—The preparation of the hydrocarbon phellandrene, of nitrophellandrene, phellandrendiamine and amidophellandrene, from *Oleum phellandrii*, was recently described (Abstr., 1886, 1038). Subsequently by similar treatment with nitrous acid, lævorotatory terebenthene has yielded a dextorotatory nitroterebenthene, $C_{10}H_{15}\cdot NO_2$, from which nascent hydrogen produces the primary base amidoterebenthene, $C_{10}H_{15}\cdot NH_2$, which again is lævorotatory. J. T.

Formation of Euxanthic Acid from Euxanthone by the Animal Organism. By S. v. Kostanecki (*Ber.*, **19**, 2918—2920).—Spiegel has proved that euxanthic acid is decomposed by concentrated sulphuric acid into euxanthone and glycuronic acid. From the phenolic character of euxanthone, and the fact that the magnesium salt of euxanthic acid, known as Indian-yellow, is prepared from urine, the author has endeavoured with success to form euxanthic acid from euxanthone, the glycuronic acid being supplied by the animal system. If euxanthone be administered to a dog, the presence of euxanthic acid can be detected in the urine by means of its magnesium salt. This result is analogous to the conversion of phenol or naphthol into their corresponding glycuronic acids by the animal organism. V. H. V.

Kamala. By A. G. Perkin and W. H. Perkin, jun. (*Ber.*, **19**, 3109—3110).—Kamala, a yellow dyestuff, is used in considerable quantity by the natives of India. It is contained in the seed capsules of *Mallotus phillipensis*, and occurs in commerce as a yellowish-brown powder, which, under the microscope, is seen to consist of transparent brown, resinous globules mixed with woody fibres and seeds; no crystals were observed.

Mallotoxin, $C_{11}H_{10}O_3$ or $C_{18}H_{16}O_5$, was obtained by shaking finely-divided kamala with carbon bisulphide, concentrating the yellowish solution on the water-bath, treating the yellowish-brown precipitate obtained with small quantities of carbon bisulphide to remove resinous impurities, and finally crystallising from benzene or toluene. It forms small, flesh-coloured needles, soluble in alkalis to a yellowish-red solution, from which acids reprecipitate the original substance; it is nearly insoluble in water, readily soluble in alcohol and acetic acid. A yellow

acetyl-derivative, $C_{11}H_8O_3Ac_2$ or $C_{18}H_{13}O_5Ac_3$, was obtained. Further experiments are in progress to determine the correct formula.

A. J. G.

Synthesis of Pyrroline. By G. Ciamician and P. Silber (*Ber.*, **19**, 3027).—The authors showed previously (Abstr., 1884, 1115) that succinimide may be readily converted into tetrachloropyrroline, but were unable to completely reduce the latter to pyrroline. This can be readily effected by Hepp's method, which consists in boiling the chloride with the corresponding amount of potassium iodide in a reflux apparatus. The iodide so obtained is very readily reduced to pyrroline by warming with potash solution in presence of zinc-dust.

N. H. M.

Behaviour of Methylketole: Constitution of Pyrroline. By G. Ciamician (*Ber.*, **19**, 3028—3029).—Ciamician and Dennstedt obtained (Abstr., 1882, 1214) pyridine-derivatives by the action of chloroform or bromoform on the potassium compound of pyrroline, and suggested that quinoline-derivatives could probably be obtained in a similar manner from indole. Experiments made by the author show that quinoline-derivatives can be obtained from methylketole by means of the chloroform reaction, and also by heating with hydrochloric acid at 200° (compare *Ber.*, **14**, 1341).

Both methylketole, and in a less degree indole, show all the colour reactions of pyrroline. The author considers the relation between indole and pyrroline to be established by these results. N. H. M.

Synthesis of Pyrroline-derivatives. By C. Paal and C. W. T. Schneider (*Ber.*, **19**, 3156—3163).—This is a continuation of the author's previous work (Abstr., 1886, 559).

Ethylene-α-tetramethyldipyrroline, $C_2H_4(C_4NH_2Me_2)_2$ [$C_2H_4 : Me_2 = 1 : 2 : 5$], was obtained by the action of acetonylacetone on ethylenediamine. It crystallises with 4 mols. H_2O in glistening, white scales, melts at 125—126°, sublimes unchanged, and is volatile in steam. It is insoluble in water, soluble in alcohol, ether, &c. It is soluble in mineral acids with red coloration, colours pine shavings carmine, and gives a purple-red with Laubenheimer's reagent. It forms a yellow *platinochloride*.

Trimethylene-α-tetramethyldipyrroline, $C_3H_6(C_4NH_2Me_2)_2$, is formed when trimethylenediamine is substituted for ethylenediamine in the above reaction. It forms a pale yellow, crystalline substance melting at 76—77°, insoluble in water, soluble in alcohol and ether. It resembles the ethylene compound in properties.

Paradiphenylene-α-tetramethyldipyrroline, $C_{12}H_8(C_4NH_2Me_2)_2$, from benzidine and acetonylacetone, crystallises in colourless tables soluble in alcohol, ether, &c. It is very unstable, especially when in solution. It melts at 130°, and is decomposed at a slightly higher temperature.

When ethyl acetophenoneacetoacetate is used in place of acetonylacetone, the ethers of a series of dipyrrolinedicarboxylic acids are obtained.

Ethyl ethylene-α-dimethyldiphenyldipyrroline-β-dicarboxylate,

$C_2H_4(C_4NHMePh\cdot COOEt)_2$ [1 : 2 : 5 : 3],

crystallises with $4H_2O$ in glistening scales melting at 197°. It distils unchanged, but is sensitive to light. It is insoluble in water and light petroleum, soluble in alcohol, benzene, chloroform and glacial acetic acid. It is insoluble in hydrochloric acid, but dissolves in concentrated nitric or sulphuric acid, and is reprecipitated unchanged on the addition of water. It shows Laubenheimer's reaction. On hydrolysis, it yields the free crystalline *acid*, which melts at 181°, and at a slightly higher temperature evolves carbonic anhydride, forming the pyrroline-derivative $C_2H_4(C_4NH_2MePh)_2$. The acid is insoluble in most solvents, very sparingly soluble in alcohol and in glacial acetic and concentrated hydrochloric acids.

β-Ethocarboxyl-α-methylphenylpyrroline-acetic acid,

$$COOH\cdot CH_2\cdot C_4NHMePh\cdot COOEt\ [1:2:5:3],$$

formed on substituting amido-acetic acid for the diamine in the last reaction, crystallises in needles melting at 131°. It is almost insoluble in water, soluble in alcohol, ether, and benzene. It dissolves in alkalis and alkaline carbonates, and forms well-characterised salts. When heated with alcoholic potash, it yields the free bibasic *acid*,

$$COOH\cdot CH_2\cdot C_4NHMePh\cdot COOH.$$

This forms small white needles which melt at 152° with evolution of carbonic anhydride.

Ethyl metaphenylene-α-dimethyldiphenyldipyrroline-β-dicarboxylate,

$$C_6H_4(C_4NHMePh\cdot COOEt)_2,$$

crystallises in white needles which melt at 185°. It is insoluble in water, soluble in most other solvents, and in concentrated sulphuric acid.

Ethyl paradiphenylene-α-dimethyldiphenyldipyrroline-β-dicarboxylate, $C_{12}H_8(NC_4HMePh\cdot COOEt)_2$, from benzidine and ethyl acetophenoneacetoacetate, crystallises in thin needles melting at 178—179°. When saponified, it yields the corresponding potassium salt, which, however, resinifies easily. The free acid could not be obtained.

β-Ethocarboxyl-α-methylphenylpyrrolinemetabenzoic acid,

$$COOH\cdot C_6H_4\cdot NC_4HMePh\cdot COOEt,$$

crystallises in small, yellow needles melting at 160°, and soluble in alcohol, ether, &c. It forms characteristic salts. When heated with alcoholic potash, it yields the corresponding bibasic *acid*, which forms colourless, hairy needles melting at 210°. When strongly heated, carbonic anhydride is evolved.

Ethyl azobenzene-α-methylphenylpyrroline-β-carboxylate,

$$N_2Ph\cdot C_6H_4\cdot C_4NHMePh\cdot COOEt,$$

from amido-azobenzene, forms deep red crystals melting at 123°. It is easily soluble in alcohol, ether, &c. When saponified, it yields the corresponding *acid*, which forms large, red crystals soluble in ether, alcohol, &c. It melts at 195°, and evolves carbonic anhydride at a slightly higher temperature.

All these substances show Laubenheimer's reaction. L. T. T.

Synthesis by Means of Ethyl Acetoacetate. By L. Knorr (*Annalen*, **236**, 290—332).—The author has already shown (Abstr., 1885, 554) that ethylic diacetosuccinate reacts with ammonia and with primary amines, yielding substituted pyrroline-derivatives. A similar action takes place with hydroxylamine. By heating an aqueous solution of hydroxylamine hydrochloride (12 parts) and sodium acetate (24 parts) with ethyl diacetosuccinate (30 parts), dissolved in glacial acetic acid, the *ethyl hydroxydimethylpyrrolinedicarboxylate*, $OH{\cdot}C_4NMe_2(COOEt)_2$, is obtained as a crystalline compound, soluble in alcohol and ether, and in dilute alkalis, but insoluble in acids. This substance melts between 98° and 100°. A precipitate of the composition $C_{12}H_{16}KNO_5$ is obtained on adding ether to an alcoholic solution of the ethyl salt and potassium ethoxide.

A mixture of hydroxydimethylpyrrolinecarboxylic acid and *monethyl hydroxydimethylpyrrolinedicarboxylate* is formed when the ethylic salt is saponified by alcoholic potash. The latter compound, $C_{10}H_{13}NO_5$, crystallises in needles, soluble in alcohol. It melts at 185°, with decomposition, yielding ethylic hydroxydimethylpyrrolinecarboxylate.

Hydroxydimethylpyrrolinecarboxylic acid,

$$C_7H_9NO_3\ [OH : Me : COOH : Me = 1 : 2 : 3 : 5],$$

decomposes at 138°, yielding hydroxydimethylpyrroline, $[OH : Me_2 = 1 : 2 : 5]$. The acid crystallises in needles, and dissolves freely in alcohol. It is decomposed by prolonged boiling with water. The metallic salts are not characteristic. The formation of the ethyl salt has just been mentioned. Hydroxydimethylpyrroline exhibits the pinewood reaction. It is soluble in alcohol, ether, chloroform, benzene and alkalis. It reduces ammoniacal silver solutions at the ordinary temperature, and Fehling's solution on boiling.

The derivatives of trimethylpyrrollinedicarboxylic acid,

$$[Me_3 : (COOH)_2 = 1 : 2 : 5 : 3 : 4],$$

phenyldimethylpyrrolinedicarboxylic, and β-naphthyldicarboxylic acid have been previously described by the author (Abstr., 1885, 555). These acids are decomposed when heated, yielding pyrrolines. *Trimethylpyrroline* [1 : 2 : 5] boils at 173° (corr.); *phenyldimethylpyrroline* [Ph : Me_2 = 1 : 2 : 5], melts at 51°, and boils at 252° (corr.), and *β-naphthyldimethylpyrroline*, [$C_{10}H_7$: Me_2 = 1 : 2 : 5], melts at 71°, and boils at 341° (corr.). These compounds are freely soluble in alcohol, ether, chloroform, and benzene.

α-Naphthyldimethylpyrrolinedicarboxylic acid, $[C_{10}H_7^{\alpha} : Me_2 : (COOH)_2 = 1 : 2 : 5 : 3 : 4]$, crystallises in needles, and decomposes at 244°, yielding *α-naphthyldimethylpyrroline*. This substance melts at 123°, boils at 310—315° (corr.), and dissolves freely in ether, alcohol, and chloroform.

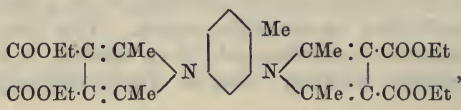
Ethyl α-naphthyldimethylpyrrolinedicarboxylate melts at 91—92°. The potassium salt, $C_{18}H_{13}K_2NO_4$, is insoluble in alcohol. The barium, $C_{18}H_{13}BaNO_4$, and silver, $C_{18}N_{14}AgNO_4$, salts, are crystalline.

Ethyl methylphenylamidodimethylpyrrolinedicarboxylate is obtained

as an uncrystallisable oil by the action of ethyl diacetosuccinate on methylphenylhydrazine. The free acid, $C_{15}H_{16}N_2O_4$, crystallises in prisms, and decomposes at 231° into carbonic anhydride and *methylphenylamidodimethylpyrroline*, $C_{13}H_{16}N_2$, a crystalline substance, which melts at 41° and boils at 310° (corr.).

Ethyl metamidotolyldimethylpyrrolinedicarboxylate, is formed by boiling equivalent quantities of metatoluylenediamine and ethyl diacetosuccinate in acetic acid solution. The ethyl salt crystallises in prisms and melts at 134°. The free acid, $C_{15}H_{16}N_2O_4 + 2H_2O$, crystallises in plates of a yellow colour. It is soluble in alcohol, ether, acids, and alkalis. It decomposes at 203°, yielding *metamidotolyldimethylpyrroline*. This compound melts at 73°, and boils at 322° (corr.) It is soluble in alcohol, ether, and acids, and volatilises in a current of steam.

Ethyl toluylenedidimethylpyrrolinedicarboxylate,



is obtained as a heavy oil by the action of metatoluylenediamine (m. p. 99°) on excess of an acetic acid solution of ethyl diacetosuccinate. The free acid, $C_{23}H_{22}N_2O_8$, is sparingly soluble in alcohol and ether, and insoluble in water and dilute acids. It melts at 248° with decomposition.

Dimethylpyrrolinedicarboxylacetic acid,

$$C_{10}H_{11}NO_6 = C_4NMe_2(COOH)_2{\cdot}CH_2{\cdot}COOH\ [2:5:3:4:1],$$

splits up at 214°, yielding carbonic anhydride and an oily liquid, probably *dimethylpyroline-acetic acid*, $C_4NH_2Me_2{\cdot}CH_2{\cdot}COOH$. The acid forms crystalline potassium and silver salts, $C_{10}H_8K_3NO_6$ and $C_{10}H_9Ag_2O_6$. The ethyl salt is prepared by boiling an acetic acid solution containing equivalent quantities of glycocine and ethyl diacetosuccinate.

Ethyl dimethylpyrrolinedicarboxylate, $C_4NHMe_2(COOEt)_2[2:4:3:5]$, is most conveniently prepared by adding a strong solution of sodium nitrite (2 parts) to 7 parts by weight of ethyl acetoacetate, dissolved in strong acetic acid. 25 parts of zinc-dust is added to the well-cooled product. On adding water to the mixture, the ethyl salt is deposited in needle-shaped crystals. This substance melts at 134—135°, and is distinguished from its symmetrical isomeride by the absence of basic properties. Many of the properties of this compound and of its derivatives have been already described by the author (Abstr., 1884, 1368). Monethyldimethylpyrrolinedicarboxylate melts with decomposition at 202° (not 200° as previously stated), forming ethyl dimethylpyrrolinecarboxylate.

Dimethylpyrrolinedicarboxylic acid decomposes at 260° into carbonic anhydride and dimethylpyrroline [Me : Me = 2 : 4] (*loc. cit.*).

Ethyl dimethylpyrrolineanilidocarboxylate,

$$COOEt{\cdot}C_4NHMe_2{\cdot}CONHPh\ [5:2:4:3],$$

is formed by the action of zinc-dust on equivalent quantities of acetoacetic anilide and ethylic nitrosoacetoacetate dissolved in acetic acid. It melts at 216°, and dissolves in hot alcohol and acetic acid. On treatment with strong sulphuric acid, it yields 2 : 4 dimethylpyrroline, and on boiling with alcoholic potash it is converted into the *monanilide* of *dimethylpyrrolinedicarboxylic acid*, $COOH{\cdot}C_4NH{\cdot}Me_2{\cdot}CONHPh$. This substance softens at 180°, and decomposes at 198°. It also splits up when boiled with dilute sulphuric acid, yielding carbonic anhydride and *dimethylpyrrolinecarboxylanilide*, $C_4NH_2Me_2{\cdot}CONHPh$.

Ethyl dimethylpyrrolineanilidocarboxylate [Me_2 : COOEt : CONHPh = 2 : 4 : 3 : 5], is prepared by reducing with zinc-dust an acetic acid solution of ethylic acetoacetate and nitrosoacetoacetic anilide. It crystallises in needles, melts at 180°, and yields 2 : 4 dimethylpyrroline on treatment with sulphuric acid.

Dimethylpyrrolinedicarboxylanilide,

$$C_4NH{\cdot}Me_2(CONHPh)_2\ [2:4:3:5],$$

is formed by reducing a mixture of the anilides of acetoacetic and nitrosoacetic acids. It melts about 255°, and crystallises in needles. It also yields 2 : 4 dimethyl pyrroline when warmed with sulphuric acid.

W. C. W.

Action of Chlorine on Pyridine. By E. H. Keiser (*Amer. Chem. J.*, **8**, 308—315).—Anderson has worked on this subject (*Annalen*, **105**, 340). When anhydrous pyridine is treated with dry chlorine, it finally solidifies, and by distillation a white crystalline solid boiling at 130°, and a yellow solid boiling at 218°, are obtained. The first is purified by crystallisation from alcohol; it melts at 72°, is very stable, and with platinum chloride gives a precipitate having the composition $(C_5H_3Cl_2N)_2,H_2PtCl_6$. The second substance cannot be distilled without partial decomposition; it is very deliquescent, and is soluble in water; with platinum chloride, the solution gives a precipitate of pyridine platinochloride; the yellow compound itself has the composition C_5H_5NCl, and is evidently an unstable additive product.

When chlorine is passed into pyridine diluted with its own bulk of water, nitrogen and carbonic anhydride are evolved, and on further dilution a white precipitate is thrown down, which when dry smells like bleaching powder, and with platinum chloride gives a precipitate of pyridine platinochloride; it is therefore an additive product of pyridine, probably the hypochlorite, and the carbonic anhydride and nitrogen are derived from the decomposition of this substance. When chlorine is passed into a pyridine solution containing free alkali, nitrogen is evolved with explosive violence, but if the contents of the flask be kept cool the action is more gentle, and chloroform and dichloracetic acid are to be found in the distillate. This decomposition of pyridine by chlorine is far more readily explained by Riedel's formula (Abstr., 1883, 1152) than by Körner's.

H. B.

Tetrahydropicoline. By A. Lipp (*Ber.*, **19**, 2843—2844).—The base obtained by the action of alcoholic ammonia on ω-bromobutyl methyl ketone (Abstr., 1886, 219) proves to be a *tetrahydropicoline*,

probably, $CH_2<\begin{matrix}CH_2—CH_2\\NH—CMe\end{matrix}>CH$. Under similar conditions, a pyrroline-derivative is obtained from ω-bromopropyl methyl ketone.

W. P. W.

Quinolinesulphonic Acids. By A. Claus and P. Küttner (*Ber.*, **19**, 2882—2886).—Quinolineorthosulphonic acid in cooled aqueous solution forms a yellow, crystalline precipitate with bromine, an unstable, probably additive, compound; at the temperature of the water-bath, the acid is decomposed with formation of tribromoquinoline, which separates in glistening, silky needles melting at 198°, soluble in ether and alcohol, insoluble in water.

Quinolineparasulphonic acid, under similar conditions, yields a dibromoquinoline, crystallising in long needles, melting at 124—126°, and yielding, on oxidation with potassium permanganate, a bromopyridinedicarboxylic acid identical with that described by Claus and Collischon. On adding more than two molecular proportions of bromine, a tribromoquinoline is slowly produced, isomeric with the compound described above. It crystallises in long, silky needles, melting at 170°, and is sparingly soluble in cold ether, soluble in alcohol. As regards the displacement of the sulphonic group, concentrated nitric acid resembles bromine in its action, a mononitroquinoline being produced.

V. H. V.

Reduction of Hydroxylepidine and Methyllepidone. By L. Knorr and C. Klotz (*Ber.*, **19**, 3299—3303).—Hydroxylepidine and methyllepidone resist the action of acid reducing agents, but are readily attacked and reduced by sodium amalgam and alcohol, or by sodium and alcohol.

Reduction of Hydroxylepidine.—When hydroxylepidine in alcoholic solution is shaken with an excess of sodium amalgam, a compound, $(C_{10}H_{10}NO)_2$, is obtained, insoluble in water, alkalis, and alcohol, but crystallising from acetic acid in slender needles melting at 280°. It shows feebly basic properties, and is most probably a diquinolyl-derivative.

The reduction proceeds further when metallic sodium is employed, and from the product, after removal of the alcohol, two compounds are obtained, one of which, *tetrahydrolepidine*, $C_{11}H_{13}N$, is separated by distillation with steam. It is a colourless, strongly refractive oil, has a pungent odour and boils at 250—253° (thermometer immersed in the vapour) at 740 mm. pressure. *Dihydrohydroxylepidine*, $C_{10}H_{11}NO$, separates in needles from the residual liquor left after steam distillation, melts at 101°, and is insoluble in alkali, sparingly soluble in water, readily soluble in alcohol, ether and chloroform. It shows feebly basic properties, and its salts are decomposed by water. Nitrous acid is without action in the cold, but on warming acts on it and forms an acid compound.

Reduction of Methyllepidone.—Sodium amalgam reduces methyllepidone, in cold alcoholic solution to the diquinolyl-derivative $(C_{11}H_{12}NO)_2$ (this vol., p. 159). It is insoluble in water, alkalis, and alcohol, soluble in acetic and hydrochloric acids, and melts at 268°. When metallic sodium is employed as the reducing agent,

dimethyltetrahydroquinoline, $C_{11}H_{15}N$, is obtained. It is a colourless oil speedily turning brown when exposed to air, boils at 255° (thermometer immersed in vapour) at 757 mm. pressure, and is identical with the base obtained by the reduction of lepidine methiodide with tin and hydrochloric acid. It yields a yellow platinochloride, and an oily, orange-red nitroso-compound.

Reduction of Carbostyril.—Tetrahydroquinoline is obtained when carbostyril in alcoholic solution is reduced with metallic sodium.

W. P. W.

α- and γ-Ethylquinoline. By L. Reher (*Ber.*, **19**, 2995—3002). —When quinoline ethiodide is heated at 280—290° for two hours, a somewhat complicated reaction takes place resulting in the formation of hydrocarbons in addition to basic products. After acidifying, the product is distilled with steam to remove the hydrocarbons, then rendered alkaline, and again steam-distilled. The mixture of bases so obtained is fractionated, and the portion boiling between 240 and 280°, after removing the unaltered quinoline, is repeatedly fractioned; in this way, fractions boiling at 255—260° and 270—275° are obtained, which consist of α- and γ-ethylquinoline respectively, but by this method, the only feasible one, a complete separation cannot be effected.

α-Ethylquinoline is a very hygroscopic, colourless liquid with a quinoline-like odour, does not solidify at low temperatures, and is slightly soluble in water, readily soluble in ether, alcohol, chloroform, and carbon bisulphide, and quickly becomes coloured red on exposure to light. The *hydrochloride* and *nitrate* are readily soluble in water, and effloresce in air. The *mercuriochloride*, $C_{11}H_{11}N,HHgCl_3$, melts at 118°, and forms slender white needles; the *platinochloride*, $(C_{11}H_{11}N)_2,H_2PtCl_6$, melts at 190°, and crystallises in dense tables; the *aurochloride*, $C_{11}H_{11}N,HAuCl_4$, melts at 142°, and forms canary-yellow needles; the *picrate*, $C_{11}H_{11}N,C_6H_2(NO_2)_3{\cdot}OH$, melts at 146—147°, and crystallises in long, yellow needles; and in addition a crystalline *stannochloride*, $(C_{11}H_{11}N)_2,H_2SnCl_4 + 2H_2O$, and an oily chromate and zinc salt are described. On oxidation, an acid was obtained agreeing in its properties with quinaldinic acid.

Tetrahydro-α-ethylquinoline, $C_{11}H_{15}N$, is formed when α-ethylquinoline is reduced with tin and hydrochloric acid. It boils at 259—263°, and resembles the parent base in appearance and odour. The *hydrochloride* crystallises in white needles which remain unaltered in air.

The fraction boiling between 270° and 275° consisting chiefly of γ-ethylquinoline, contained a diethylquinoline which was separated by means of its mercuriochloride; this salt, $C_9H_5NEt_2,HHgCl_3$, melts at 116° and crystallises in needles. *γ-Ethylquinoline* resembles the α-base in appearance and odour, and its salts show a great similarity to those of α-ethylquinoline, but have a higher melting point. The *hydrochloride* is very soluble in water and is deliquescent; the *nitrate*, $C_{11}H_{11}N,HNO_3$, melts at 115·5°, and crystallises in white needles, which become brown on exposure to air, and are soluble in water and alcohol. The *mercuriochloride*, $C_{11}H_{11}N,HHgCl_3$, melts at 154°, crystallises in white needles, and is readily soluble in water containing

hydrochloric acid; the *platinochloride*, $(C_{11}H_{11}N)_2,H_2PtCl_6$, melts at 204°, and forms brown leaf-like crystals; the *picrate* melts at 178—186° with decomposition, and forms long, yellow needles; and the *aurochloride*, $C_{11}H_{11}N,HCl(AuCl_3)_2$, forms slender, yellow needles. The *methiodide* melts at 149° and formed yellow crystals. On oxidation, cinchonic acid is obtained. γ-Ethylquinoline on reduction yields a base boiling between 271° and 275°, the hydrochloride of which is not crystalline. *γ-Ethylquinolinesulphonic acid*, $C_{11}H_{10}N\cdot SO_3H$, is obtained by heating γ-ethylquinoline at 260° with 10 times its weight of fuming sulphuric acid. It forms slender lustrous needles, melts above 315°, and is insoluble in alcohol, but readily soluble in hot water.

The hydrocarbon separated from the ethyl bases by steam distillation was fractionated, and from the lowest fraction, 210—240°, white crystals were obtained which had a strong naphthalene-like odour, and were almost certainly naphthalene. W. P. W.

Colour Reaction of Guanine. By E. v. Brücke (*Monatsh. Chem.*, **7**, 617—620).—It has long been known that guanine when evaporated with nitric acid gives a yellow residue, soluble in potash with yellow coloration; the solution thus obtained, on evaporation to dryness, gives at first a purple then a violet coloration; on exposure to air the original colour returns. In this paper, it is shown that these changes are due not to the so-called metachromatism, but to the proportion of water present; thus there exist two compounds, the one, golden-red with the greater, the other, indigo-blue, with the less proportion of water. It is not improbable that an intermediate purple-red compound is also formed. Experiments, confirmatory of this view, are described, in which the coloured solutions are exposed to conditions of the presence and absence of water respectively.

V. H. V.

Opium Alkaloïds. By P. C. Plugge (*Arch. Pharm.* [3], **24**, 993—1014).—Morphine, codeïne, thebaïne, papaverine, narcotine, and narceïne are the most important opium alkaloïds. Their physiological action varies from strongly narcotic or sleep-inducing, to strongly exciting or cramp-producing, but different observers are not agreed as to the exact order of the members of the series. In the arrangement of the bases according to their poisonous nature, different observers are more nearly in accord. The author examined the reactions of salts of these alkaloïds with alkaline salts of organic acids. Morphine, codeïne, and thebaïne, in neutral liquids, react strongly alkaline to litmus, and afford stable salts. Narcotine, papaverine and narceïne, on the contrary, do not affect litmus-paper, and combine only feebly with acids. Thus narceïne sulphate and chloride are slowly decomposed by cold water, more quickly by hot water. It appeared probable from this that solutions of salts of the stronger bases would give no precipitate with alkaline salts of organic acids, whilst in the case of the weak bases, the alkaloïd would be precipitated as such. The following salts were employed: sodium and ammonium acetate, ammonium oxalate, sodium salicylate, sodium potassium tartrate, sodium benzoate and hydrogen sodium carbonate.

Besides the six opium bases, many other alkaloïds were examined in the course of the investigation, such as caffeïne, cocaïne, atropine, pilocarpine, coniine, strychnine, brucine, quinine, cinchonine, and cinchonidine, the latter, however, only with sodium acetate. None of these bases were liberated and precipitated; in the case of the cinchona bases, however, it was necessary to carefully neutralise the sodium acetate with acetic acid, or precipitation took place. With a perfectly neutral solution of sodium acetate, the only alkaloïds precipitated are the three weak opium bases, papaverine, narcotine and narceïne. These three bases are also precipitated both by slightly acid and by slightly alkaline acetate solution. Neither of the two solutions exerts any influence on the strong opium bases, consequently the ordinary non-neutralised acetate solution can be used for the separation of the bases with advantage in point of time and perhaps completeness. Narcotine, papaverine and narceïne were precipitated as pure bases by all the alkaline salts mentioned previously. Thebaïne was precipitated by sodium salicylate as salicylate and by hydrogen sodium carbonate. Morphine and codeïne were not precipitated by any of the salts. Arranging the alkaloïds in series according to their molecular weights, it will be seen that the first three are strong bases and the last three feeble ones: morphine, $C_{17}H_{10}NO_3$; codeïne, $C_{18}H_{21}NO_3$; thebaïne, $C_{19}H_{21}NO_3$; papaverine, $C_{21}H_{21}NO_4$; narcotine, $C_{22}H_{23}NO_7$; narceïne, $C_{22}H_{29}NO_9$. Slightly acidified sodium acetate solution will indicate as little as 1 : 40,000 of narcotine in solution. With papaverine, the limit is 1 : 30,000. Narceïne is not nearly so sensitive, the limit being about 1 : 600. The precipitation of thebaïne as salicylate gave a limit of about 1 : 2000. For quantitative estimation, narcotine is best precipitated by ammonia, where it is the only substance thrown down by this reagent; sodium acetate has, however, the advantage of precipitating it for qualitative purposes from faintly acid solutions in which all other alkaloïds, excepting papaverine and narceïne, remain in solution. Papaverine and narceïne are also best precipitated quantitatively by ammonia.

J. T.

Cinchona Alkaloïds. By W. J. Comstock and W. Koenigs (*Ber.*, **19**, 2853—2859).—From considerations based on its chemical behaviour, the authors have adopted the formula $C_{19}H_{22}Br_2N_2O$ for *cinchonine dibromide* instead of that given in their previous paper (Abstr., 1885, 910). A crystalline *sulphate* is obtained by allowing a solution of cinchonine dibromide in 7 to 8 parts of concentrated sulphuric acid to remain for several hours. It is soluble in hot water and dilute alkalis, excess of alkali throwing out the salt, but dilute acids dissolve it with difficulty. When heated at 130° in a sealed tube with hydrogen bromide, it is decomposed into cinchonine dibromide and sulphuric acid.

Dehydrocinchonine, $C_{19}H_{20}N_2O$, is obtained in practically colourless needles by heating cinchonine dibromide with alcoholic potash in a reflux apparatus for 16 to 20 hours, distilling off three-fourths of the alcohol, and adding water to the residue. It is purified by precipitating its hydrochloride with ammonia, and crystallising from alcohol. The base melts at 202—203°, and sublimes without decom-

position if the temperature be carefully raised. It dissolves easily in alcohol, acetone, and chloroform, less easily in ether and hot benzene, and is practically insoluble in water. The *hydrobromide*, $C_{19}H_{20}N_2O,HBr$, crystallises from water in colourless, transparent prisms, the *hydrochloride* in long, silky needles.

Dehydrocinchonine chloride, $C_{19}H_{19}N_2Cl$, is prepared by treating dehydrocinchonine hydrochloride with phosphorus pentachloride and phosphoric oxychloride, adding ammonia, and crystallising from benzene. It melts at 148—149°, and is readily soluble in benzene, alcohol, acetone, chloroform, and ether, but insoluble in light petroleum.

Dehydrocinchene, $C_{19}H_{18}N_2$, is obtained by boiling dehydrocinchonine chloride with alcoholic potash for 16 hours, and is purified by recrystallising its hydrogen tartrate. The free base crystallised from dilute alcohol, forms long, colourless needles which melt at about 60°, and contain at least 3 mols. H_2O. The *hydrobromide*, $C_{19}H_{18}N_2,2HBr$, is obtained in small, broad, transparent, concentrically-grouped prisms which dissolve readily in water, but only sparingly in alcohol and ether. The *platinochloride*, $C_{19}H_{18}N_2,H_2PtCl_6$, a very sparingly soluble salt, is obtained in bright red tables from the solution of the base in concentrated hydrochloric acid.

Cinchene dibromide, $C_{19}H_{20}Br_2N_2$, is best prepared by gradually adding bromine to a solution of cinchene in chloroform until the yellow perbromide begins to separate, sodium hydrogen sulphite and hydrochloric acid are added, and the base precipitated from the separated aqueous layer by ammonia, is purified by conversion into the hydrobromide, &c. From its ethereal solution, it is obtained in beautiful, colourless crystals which begin to fuse at 110° and melt at 113°. The *hydrobromide* crystallises in concentrically-grouped, colourless needles; the *nitrate* and *zincochloride* also crystallise well. Boiling for 20 hours with alcoholic potash converts cinchene dibromide into dehydrocinchene. W. P. W.

Strychnine. By W. F. Loebisch and P. Schoop (*Monatsh. Chem.*, **7**, 609—616).—The products obtained on distilling strychnine with zinc-dust vary according to the temperature; at a lower temperature, one atom of oxygen is removed from the molecule with formation of a compound, $C_{21}H_{22}N_2O$, a solid substance, soluble in alcohol with a blue fluorescence, sparingly soluble in dilute acids, insoluble in water. It does not give the strychnine reaction with potassium dichromate and sulphuric acid. At a higher temperature, the strychnine molecule is completely decomposed; hydrogen, ethylene, acetylene, and ammonia are evolved, whilst carbazole distils over. Similarly brucine and the acid, $C_{16}H_{18}N_2O_4$, obtained by the oxidation of strychnine with chromic acid, yield carbazole on distillation with zinc-dust. On dry distillation, strychnine yields the same gaseous products, but only comparatively small quantities of carbazole, accompanied probably by pyrroline. V. H. V.

Specific Rotation of Piperidine Bases. By A. Ladenburg (*Ber.*, **19**, 2975—2977).—Completing his recent research on the

specific rotation of piperidine bases (this vol., p. 164), the author finds for α-pipecoline $[\alpha]_D = 21{\cdot}74°$, and for α-ethylpiperidine $[\alpha]_D = 6{\cdot}75°$. α-Isopropylpiperidine and β-pipecoline do not yield optically active bases by conversion into dextrotartrates. From the mother-liquor of the α-pipecoline hydrogen tartrate the lævorotatory base was obtained; but this, even after conversion into the hydrochloride and treatment with cadmium iodide to remove any accompanying dextrorotatory base, gave only a specific rotation of −19°, and probably contained either the dextrorotatory or the inactive base as impurity which could not be separated. Experiments show that the inactive piperidine bases are compounds and not mixtures of the optically active modifications; and therefore it has been possible to effect a decomposition into two optically active salts only in those cases where the temperature employed in the crystallisation lay above or below the transition temperature of the inactive hydrogen dextrotartrate (comp. Abstr., 1886, 968).

The unexpectedly low specific rotation of the dextrorotatory α-ethylpiperidine renders it probable that the specimen employed was not pure. W. P. W.

Alkaloïds of the Berberideæ. By O. Hesse (*Ber.*, **19**, 3190—3194).—The author has re-investigated the alkaloïds in the root of *Berberis vulgaris*. He believes that there are therein at least four alkaloïds besides berberine, and describes especially oxyacanthine (Wacker, *Chem. Centr.*, 1861, 321), and a new alkaloïd he has obtained from the mother-liquors of oxyacanthine, and which he names *berbamine*.

He finds the true formula of oxyacanthine to be $C_{18}H_{19}NO_3$ and not $C_{19}H_{21}NO_3$, as he has previously given. When crystallised from water and dried at 100°, this alkaloïd melts at 138—150°, but when crystallised from alcohol or ether, it forms needles melting at 208—214°. It is easily soluble in chloroform, and then gives $[\alpha]_D = +131{\cdot}6°$ ($p = 4$, $t = 15°$). In light petroleum and alkalis, it is only slightly soluble, and ether extracts it completely from the alkaline solutions. The *hydrochloride*, $C_{18}H_{19}NO_3,HCl + 2H_2O$, forms small colourless needles which in aqueous solutions give $[\alpha]_D = +163{\cdot}6°$ ($p = 2$, $t = 15°$). The *platinochloride* is a yellow, flocculent precipitate. The *nitrate* and *sulphate* are both crystalline. When heated with potash and a little water, the base melts to a brown mass which floats on the surface of the fused potash. This brown mass is the potassium compound of *β-oxyacanthine*. This conversion into a β-modification also takes place very readily, even at ordinary temperatures, when the alkaloïd is acted on by alkalis or barium hydroxide in the presence of alcohol. Ether now no longer extracts the alkaloïd from the alkaline solution. Hydrochloric acid precipitates β-oxyacanthine, which is soluble both in alkalis and in excess of acid. If, however, the alkaline solution of the β-compound is supersaturated with hydrochloric acid, α-oxyacanthine hydrochloride crystallises out. The author believes the β-modification is due to the alkaloïd taking up an additional molecule of water. Oxyacanthine very closely resembles narcotine in properties.

Berbamine crystallises in small scales of the composition $C_{18}H_{19}NO_3 + 2H_2O$. It is easily soluble in ether. When anhydrous, it melts at 156°. The *hydrochloride* crystallises in scales, the *nitrate* in needles; the *platinochloride* forms a yellow crystalline precipitate.

L. T. T.

Colchicine. By S. Zeisel (*Monatsh. Chem.*, **7**, 557—597).—Previous observations on the composition and properties of colchicine have, for the most part, been very discordant; in this paper, a long summary is given. The principal results obtained by the author are as follows: the composition of colchicine is expressed by the formula $C_{22}H_{25}NO_6$; it combines with chloroform to form a crystalline compound, $C_{22}H_{25}NO_6,2CHCl_3$, readily decomposed by water into its components. Colchicine is slightly basic, but its salts, with the exception of an aurochloride, $C_{22}H_{25}NO_6,HAuCl_4$, cannot be obtained from their aqueous solutions. Colchiceïne, formed from colchicine, when heated with a trace of hydrochloric or sulphuric acid, has the composition $2C_{21}H_{23}NO_6,H_2O$. As the difference between the two compounds is one CH_2 or methylene group, and as methyl alcohol is produced in the decomposition, it follows that colchiceïne is a demethylated colchicine.

Colchiceïne possesses at once the properties of a base, as evidenced by the formation of an aurochloride, $C_{21}H_{23}NO_6,HAuCl_4$, and also those of a monobasic acid, or more probably of a phenol, as shown by the formation of a copper derivative $(C_{21}H_{22}NO_6)_2Cu$, and by the readiness with which it dissolves in alkalis. As colchicine has no acidic properties, it is probably a methoxy-derivative of a compound, of which colchiceïne is the corresponding hydroxy-derivative.

It is suggested that the molecular formula of each of the above substances is the double of that given; owing to the complex composition of the substances, the number of hydrogen-atoms is given with a certain reserve.

V. H. V.

Ecgonine. By C. E. Merck (*Ber.*, **19**, 3002—3003).—The author has repeated an experiment made by Calmels and Gossin (Abstr., 1885, 912), and finds that ecgonine when distilled with almost dry barium hydroxide yields methylamine and not ethylamine as one of the products; this corresponds with the behaviour of tropine under like conditions. When ecgonine hydrochloride is heated with an equal weight of phosphorus pentachloride and 10 parts of chloroform at 100° for 10 hours, a base is obtained which yields a well crystallised aurochloride, $C_9H_{13}NO_2,HAuCl_4$, corresponding with ecgonine less the elements of 1 mol. H_2O. The base has not yet been obtained in the pure state.

W. P. W.

A New Ptomaïne producing Tetanus. By L. Brieger (*Ber.*, **19**, 3119—3121).—The author has already described an alkaloïd, tetanine, obtained in the cultivation of Rosenbach's microbe. The beef extract in which the microbe had been cultivated for four to six weeks, was acidified with hydrochloric acid, boiled, and filtered; the filtrate evaporated and treated with lead acetate and alcohol, filtered, and the lead removed as far as possible as chloride, and finally as

sulphide. The strongly alkaline filtrate was distilled with steam, acidified with hydrochloric acid, evaporated to dryness, and treated with alcohol to remove ammonium chloride. After removing the alcohol, the new base was separated as its aurochloride.

The free base, $C_5H_{11}N$, is volatile, boils about 100°, but was not obtained free from water. The *hydrochloride* is crystalline, melts at 205°, and is very readily soluble in water and absolute alcohol. The *aurochloride*, $C_5H_{11}N,HAuCl_4$, crystallises in plates, and melts at 130°. The *platinochloride*, $(C_5H_{11}N)_2,H_2PtCl_6$, crystallises in plates, is decomposed at 240°, and is sparingly soluble in water. The picrate crystallises in readily soluble needles. The base gives a yellow precipitate with phosphomolybdic acid, a white precipitate with phosphotungstic acid, and a red crystalline precipitate with potassium bismuth iodide. Injected hypodermically in a comparatively large dose, it produces the symptoms of tetanus. A. J. G.

Albumoses. By R. Neumeister (*Zeit. Biol.*, **23**, 381—401).—The question investigated in this research was whether or not each albumose was converted into isomerides belonging to the anti- and hemi-groups of digestion products.

The method previously described by Kühne and Chittenden of separating proto- from deutero-albumose is not a satisfactory one. Hetero-albumose is easily separated by its being precipitated when the salts are dialysed out from a mixture of the albumoses. It can also be separated from the mixture by saturating it with sodium chloride; part of the proto-albumose and the whole of the deutero-albumose remain in solution. In the precipitate, hetero-albumose can be separated by dialysis as before. By acidifying the filtrate, which contains the deutero-albumose and part of the proto-albumose, the proto-albumose and about half the deutero-albumose are precipitated; this is filtered off; the deutero-albumose remaining in solution is not mixed with any other albumose; the sodium chloride is dialysed off, the fluid is saturated with ammonium sulphate, and thus the peptone alone is left in solution; the precipitate of deutero-albumose is redissolved and obtained free from ammonium sulphate by dialysis, and finally precipitated by alcohol. It gives no precipitate with copper sulphate; previous statements that such a precipitate occurs were due to its admixture with proto-albumose.

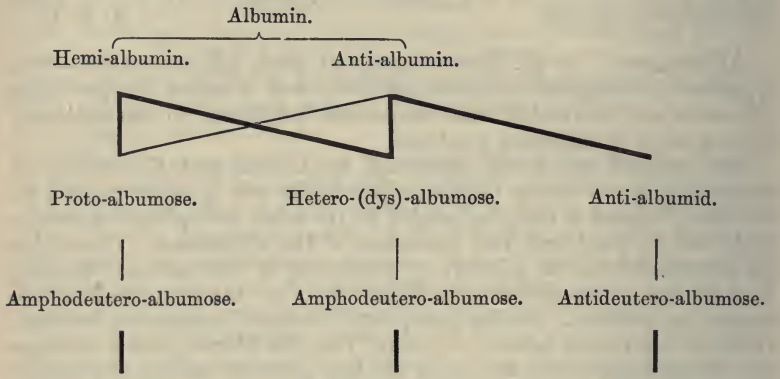
On prolonged heating of proto-albumose with 5 per cent. sulphuric acid, deutero-albumose is formed. Hetero-albumose yields the same substance, and also anti-albumid. The same result is obtained on peptic digestion, and also on tryptic digestion, more rapidly in the latter case than the former. The formation of the so-called globulin-like substance does not occur in tryptic digestion.

No deutero-albumose is formed directly from fibrin; but proto- and hetero-albumose are intermediate products in its formation, both by acids and by ferments.

Anti-albumid yields deutero-albumose also, and seems to be largely a bye-product of the formation of hetero-albumose. The deutero-albumose obtained is an anti-product yielding only anti-peptone; much insoluble anti-albumid is left after prolonged digestion, which will

yield no more albumose. This insoluble substance swells with sodium hydroxide; it is turned yellow by nitric acid, and orange on the subsequent addition of ammonia; in its solubilities it much resembles keratin.

The deutero-albumose formed from proto- and hetero-albumose is called ampho-deutero-albumose, as it is subsequently converted into amphopeptone (that is, hemi- and anti-peptone); the anti-products from proto-albumose are, however, exceedingly small in quantity, and the author suspects that his method of preparing proto-albumose does not give him that substance quite free from traces of hetero-albumose; and that perfectly pure proto-albumose will be found to be a pure hemi-albumose. The changes in the digestion of albumin are represented in the following schemes.



W. D. H.

Vitelloses. By R. Neumeister (*Zeit. Biol.*, **23**, 402—411).—Following on the lines of Kühne and Chittenden, the products of the digestion of vitellin have been subjected to analysis. The variety of the proteïd employed was plant vitellin (phytovitellin), prepared from pumpkin seed.

Coagulated vitellin was found to be the best to employ; in peptic digestion, syntonin was formed as one product. This resembled ordinary acid albumin, except that it was insoluble in strong nitric acid, and gave the biuret reaction, not the ordinary purple colour. A substance, antivitellid, corresponding with anti-albumid, was also formed, but no coagulable substance like that obtained in the peptic digestion of globulin.

The ultimate products of digestion are peptones; vitellose is the name given to the intermediate products: proto-, hetero-, deutero- and dysvitellose, which correspond with the albumoses with similar prefixes. These may be separated from one another and from peptones as the albumoses are.

Protovitellose becomes deuterovitellose on further peptic digestion: when subjected to the action of the tryptic ferment, a trace of antivitellid

is formed; the end products are antipeptone, tyrosine, leucine, and the substance which becomes violet with bromine.

Heterovitellose and dysvitellose, derived from it, do not differ in their properties from the analogous albumoses; under tryptic digestion, much antivitellid is formed, the end product being antideuterovitellose. Under prolonged peptic digestion, amphodeuterovitellose is formed.

The anti- and ampho-varieties of deuterovitellose correspond with the similarly named albumoses. W. D. H.

Physiological Chemistry.

Gases of Parotid Saliva. By R. Kulz (*Zeit. Biol.*, **23**, 321—328).—Observations on the gases of human saliva have not been previously made. The saliva was obtained by means of a gum elastic canula (which was found to be better than the metal one at first used) inserted into Stenson's duct; the saliva was collected over mercury to obviate the danger of absorption of atmospheric air.

As the mean of 11 analyses, the total quantity in volume from 100 c.c. of saliva was 7 c.c. of gas, of which 1 c.c. was oxygen, 2·5 nitrogen, and 3·5 c.c. carbonic anhydride. By the addition of phosphoric acid, a large amount (40—60 per cent.) of carbonic acid contained in the saliva as carbonates was obtained. The amount of oxygen and nitrogen in the saliva exceeds that in the blood-serum.

With regard to the carbonic anhydride present, and the alkalinity of the secretion which is due to the carbonates, it is found that food in the stomach does not alter the reaction of the saliva as it does that of the urine. After an abundant secretion of gastric juice, many observers have noted, and these experiments confirm their results, that the urine becomes less acid or even alkaline. That there is no such effect on the saliva is shown both by the estimation of the carbonic acid and by titration. W. D. H.

Free Hydrochloric Acid of the Gastric Juice. By H. A. Landwehr (*Chem. Centr.*, 1886, 484).—The author has previously shown, in conjunction with Fick, that the action of this acid on diastase is inverted in the presence of peptones, in the sense that its activity is increased rather than suspended; the cause probably lying in its combination with amido-acid groups of the peptones. Calm has recently shown (*Deut. Arch. f. klin. Med.*, **23**) that in certain pathological conditions the gastric juice has the reactions rather of an organic acid than of dilute hydrochloric acid.

It is well known that lactic acid decomposes sodium chloride. That this taken place in cold dilute solution is readily seen by comparative observations of the acidity (methyl-violet being used as indicator) of a lactic acid solution before and after addition of sodium chloride.

The author applies these observations to a discussion of the origin and nature of the acidity of gastric juice, arriving at the following hypothesis :—Lactic acid is formed by fermentation from the mucus of the stomach, and, acting on alkaline chlorides, liberates hydrochloric acid, which is forthwith taken up in combination by the albuminoïds of the food. The sodium lactate is simultaneously assimilated. With the gradual peptonising of the albuminoïds, the hydrochloric acid is liberated. C. F. C.

Ferment Organisms of the Alimentary Canal. By N. Miller (*Chem. Centr.*, 1886, 580).—Of the 25 micro-organisms identified by the author in the mouth, 12 were also found in the intestines, and 8 in the stomach. Although normal gastric juice is antiseptic, the conditions in the stomach are often such as to prevent contact of the organisms therewith, which then continue active. These organisms are also carried forward into the intestines by liquids which remain only a short time in the stomach.

In most cases, these organisms exert a peptonising but only seldom a diastatic action. In some cases, they induce lactic fermentation of carbohydrate solutions; in others acetic and butyric. In some instances the fermentation was attended with the evolution of carbonic anhydride and hydrogen. C. F. C.

Formation of Fat in the Dog from Carbohydrates. By J. Munk (*Bied. Centr.*, 1886, 748—750).—A bitch was allowed to fast for 31 days, this being the period stated by Hofmann to be necessary for the removal of all fat from the system—31 per cent. of the weight was lost. The animal was then fed with 200 grams of flesh, 100 grams of gelatin, and an increasing ration of starch and sugar in equal parts (300 to 500 grams). After 25 days the animal was killed and examined, when it was found to have increased in weight at a rate of 36 grams daily, and, taking the lowest valuation, nine-tenths (960 grams) of the whole fat found in it had been put on during the 25 days. The sources from which the fat could have been formed were three: namely, fat in the flesh given, decomposed albumin, and carbohydrates. Of the fat produced by the decomposition of albumin, there would be according to Voit and Pettenkofer 12 per cent., according to Henneberg 51 per cent.—415 grams should be formed; but this quantity must be reduced to 42 to 45 per cent. if Zuntz's method of calculating Henneberg's results is to be followed; the author therefore considers that 343 to 364 grams fat must be attributed to albumin; the fat from the meat amounted to 75 grams. However, whatever may be the quantity of actual fat from albumin, there appears to be no doubt that 788 grams (max.) 470 grams or 542 to 521 grams of fat (according to the method of calculation used), had to be sought for from other sources, namely, the gelatin and starch. The author allows for argument's sake that 338 grams might come from the gelatin (this, however, according to Voit and Pettenkofer, is inadmissible), even then 162 grams of fat must have come from the carbohydrates.

E. W. P.

Relation between the Destruction of Glucose and the Production of Animal Heat and Work. By A. Chauveau and Kaufmann (*Compt. rend.*, **103**, 974—975, 1057—1064, 1153—1159).—On comparing two organs which, under ordinary physiological conditions, have very unequal thermogenic activities, it is always found that the destruction of glucose is much greater in the organ in which combustion is most active, or, in other words, the heat developed in animal tissues, which is proportional to the amount of internal combustion, is also proportional to the quantity of glucose removed from the blood in the capillaries.

Analyses of the blood of the masseter muscle and parotid gland of the horse during a state of repose, showed that the activity of combustion in the muscle as measured by the amount of oxygen absorbed and of carbonic anhydride produced is to that in the gland as 4·57 : 1, whilst the destruction of glucose is as 5·68 : 1.

During the process of mastication and insalivation, the activity of combustion in the muscle is increased by 3·5 times, whilst the consumption of glucose in the blood traversing the muscle is increased to almost the same extent. In the gland, the ratio between the activity of combustion at rest and in action is 60 : 87, whilst the consumption of glucose is as 70 : 90. In experiments of this kind, it is important to take into account not only the composition of the blood, but also the volume which traverses the organ in unit time.

Details of the method of experiment and of the analyses are given in the original papers.

Glucose is always found in the nutritive secretions, but never in any tissues except the liver. Glycogen, on the other hand, does not occur in the blood, but only in the hepatic and muscular tissues. Analyses of muscle in repose and in action confirm the statement that glycogen accumulates while the muscle is at rest, but disappears during activity. The glucose which disappears from the capillaries leaves them in company with oxygen, and is more or less completely converted into water and carbonic anhydride in the organs and tissues. The glycogen which has accumulated in the muscles provides the materials for combustion during periods of great activity when the supply of glucose is not equal to the demand. Only a portion of the glucose which disappears from the capillaries is consumed; the remainder becomes converted into muscular glycogen by dehydration, and then forms a reserve. During excessive work, the glycogen becomes hydrated and reconverted into glucose, which is consumed.

The liver is the indirect collaborator of the muscles during activity. In fact the hepatic gland performs its functions as a glycogenic organ the more actively each time that any work is done by any part of the animal economy. This is established by the fact that the blood never becomes appreciably poorer in glucose even during activity. On the contrary, there is often an excessive production of glucose, especially if the activity is localised as in mastication.

So long as the liver furnishes glucose to the blood in sufficient quantity, so long does the animal continue to develop the quantity of heat necessary for the activity of the other organs and the maintenance of the bodily temperature. When the glycogenic function of

the liver becomes enfeebled, glucose disappears from the blood-vessels, organic combustion rapidly diminishes, and death supervenes as a result of arrested calorification. C. H. B.

Origin of the Bile Colouring Matters. By H. Stern (*Chem. Centr.*, 1886, 481).—The author's experiments were performed on pigeons. The bile-ducts being ligatured and provision being made for collecting the urine separately, by ligaturing the rectum above the entrance of the urethra, it was found that within $1\frac{1}{2}$ hours the urine was highly charged with these colouring matters. After death, the tissues were found to be similarly charged. In a second series of experiments, the liver was thrown entirely out of the circulation. In this case neither in the blood, urine, nor tissues were any traces of these colouring matters found. The author concludes from his experiments that these substances originate entirely in the liver substance. C. F. C.

Active β-Hydroxybutyric Acid. By E. Kulz (*Zeit. Biol.*, **23**, 329—339).—The author has previously described the occurrence of this substance in diabetic urine. It may be prepared as follows:—Diabetic urine which gives the ferric chloride reaction and is strongly lævorotatory is (after the removal of the sugar by fermentation) concentrated to a thin syrup, and neutralised with sodium hydroxide, three times as much 95 per cent. alcohol is added, which produces an abundant precipitate; from the alcoholic filtrate, the alcohol is evaporated, and more alcohol added; this is repeated until alcohol gives no further precipitate; the last traces of alcohol are removed by shaking with ether. To the residue, sulphuric acid is added, and the mixture shaken with an equal volume of ether.

The ether is driven off by heat, and the remaining brown syrup gives a precipitate with lead acetate, which is filtered off. From the filtrate, excess of lead is removed by sulphuretted hydrogen; baryta-water is added, and the barium salt of the acid is obtained in solution. Urea is then precipitated by means of mercuric nitrate, excess of mercury being removed by treatment with sulphuretted hydrogen. From the solution of the barium salt, the silver salt is obtained by adding a solution of silver sulphate; the barium sulphate is removed, and on concentration crystals of the silver salt are obtained and purified by recrystallisation. The free acid is obtained by decomposing the solution of the silver salt with sulphuretted hydrogen. The specific rotatory power of this acid is $[\alpha]_D = -23{\cdot}4$. The ammonium salt has the specific rotation denoted by $[\alpha]_D = -16{\cdot}3$.

Minkowski's test for this acid in urine (*Arch. exp. Path. u. Pharmak.*, **18**, 41) is not regarded as trustworthy; and the obtaining of crystals of α-crotonic acid, on adding sulphuric acid, is preferred. The presence of a substance which rotates polarised light to the left, which gives the ferric chloride reaction, and which is not precipitable by lead acetate, may be taken as strong presumptive evidence of the presence of β-hydroxybutyric acid. Benzoic acid (from the decomposition of hippuric acid), salicylic acid, and phenol, might possibly be confounded with it; methods of avoiding such a mistake are given. The

acid does not appear to be present in the urine of healthy men or animals; but it occurs in unhealthy urines not only in cases of diabetes, but also in cases of scarlet fever, measles, diphtheria, scurvy, and in certain mental affections. W. D. H.

Physiological Action of Convolvulin and Jalapin. By G. Dragendorff (*Chem. Centr.*, 1886, 589).—The question of the excretion of these glucosides after being taken into the human stomach has been investigated by Bernatzik (*Wiener med. Jb.*, 1862–63); traces only were found in the fæces, none in the urine. This result was confirmed by Köhler and Zincke (*W. Jb. für Pharm.*, **32**, 1); who, however, succeeded in isolating these purgatives from the stomach and intestines. The author has repeated these investigations, adopting a simplified method of examination of the parts for the glucosides and products of decomposition (convolvulic and jalapic acids), based on extraction with chloroform. 0·5 gram of the glucosides was the quantity given, cats being taken as the subject of the experiments.

The author confirmed the previous results in regard to the non-excretion of the drugs in the fæces and urine. The animals were killed after the lapse of four hours, and the organs examined; appreciable quantities of the drugs were found in the stomach and small intestines, less in the duodenum, traces only in the lungs and pancreas. No evidence was obtained that the glucosides are converted into the derived acids. C. F. C.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Life in Relation to Oxygen. By P. Liborius (*Chem. Centr.*, 1886, 579). — The author classifies these organisms as follows:—

(1.) Exclusively anaerobic: amongst these there are many which multiply without attendant fermentation.

(2.) Exclusively aerobic: reduced to inactivity by deprivation of oxygen. This class includes:—*B. fluorscens liquifaciens*, *B. aerophilus*, *B. cyanogenus*, *B. fuscus*, *B. aquatilis fuscus*, *B. subtilis*. With exception of the first-named, which appears to determine a special fermentation of albuminoïds with formation of volatile fatty acids, the bacteria of this group have not been closely studied in relation to fermentation.

(3.) Optionally anaerobic: activity lowered, but not suspended, by deprivation of oxygen. This class includes all the pathogenic organisms: *B. anthracis*, *B. typhi abdom.* From this general view of the conditions of bacterial life, and from his own special investigations, the author concludes that an attendant fermentation is not an essential condition of anaerobic activity in the sense in which it has been so stated by Pasteur and Nägeli. C. F. C.

Wine and Brandy from Raspberries and Strawberries. By A. Rommier (*Compt. rend.*, **103**, 1266—1268).—The ferment of the raspberry, which has been described by Le Bel as *Levure wurtzii*, is not able to convert the whole of the sugar of the raspberry into alcohol. In order to ascertain if this is due to want of activity in the ferment, or to the action of some constituent of the fruit, energetic ellipsoïdal wine yeast was mixed with the liquid. Fermentation then proceeded rapidly, and not only the sugar existing in the fruit, but two or three times the quantity of added sugar, was converted into alcohol. Raspberry brandy, obtained by distilling the wine, is very aromatic, and has the odour of raspberries, then becomes slightly smoky, but finally acquires a very fine bouquet.

The ferment of strawberries is more active, but fermentation is accelerated by the addition of ellipsoïdal wine yeast. Strawberry wine from French strawberries is less acid than that from raspberries, and keeps well, provided that it contains 16 per cent. of alcohol. The brandy has a strawberry bouquet, which becomes stronger after some time, but does not alter in character.

The flavour of the brandy from English strawberries, although made with a double quantity of added sugar, is still so strong as to be unpleasant, but if diluted with water the strawberry bouquet develops in perfection, a fact which indicates that more sugar might be added with considerable advantage.

Levure wurtzii and others, such as *L. apiculatus*, have no inversive properties, and can therefore act only on invert sugar, and are unable to alter the saccharose which also exists in the juices of many fruits. A higher yield of alcohol can be readily obtained by adding an inversive ferment like the ellipsoïdal yeast of wine. C. H. B.

Zymotic Virus and Fermentation. By S. Arloing (*Compt. rend.*, **103**, 1268—1270).—The virus of gangrenous septicæmia and of symptomatic anthrax have the power of fermenting nitrogenous substances such as peptone, albumin, and yolk of egg. The products are ammoniacal compounds, with possibly indole and skatole. Hydrogen, nitrogen and carbonic anhydride are evolved, the hydrogen being present in much greater relative proportion in the gases from albumin and yolk of egg than in those from peptone. These facts confirm the analogy between zymotic virus and ferments.

The gaseous infiltration which characterises gangrenous septicæmia and symptomatic anthrax is in all probability due to the fermentation of the carbohydrates and nitrogenous compounds in the tissues.

C. H. B.

Loss of Nitrogen by Plants during Germination and Growth. By W. O. Atwater and E. W. Rockwood (*Amer. Chem. J.*, **8**, 327—343).—During the germination of seeds, and the early growth of plants, may there be a material loss of nitrogen? (compare Abstr., 1885, 1005). Peas were allowed to germinate and grow for a certain length of time in moist sand, and the nitrogen contained in them and also in the sand and moisture estimated. The sum of these two quantities was always less than the computed nitrogen in the original seeds, the loss varying from 6 to 16 per cent., according to the time

of the experiment and the locality. Only in cases where a quantity of the rootlets had been torn off in removing the plants from the sand did the nitrogen in the moist sand exceed 3 per cent. of the whole. Bearing in mind the work of other experimenters, the authors believe that this loss of nitrogen, which is not observed in the germination of all seeds, is not a normal process of the growth of the plant, but is caused by processes of decomposition that depend on the presence of microbes. H. B.

Variations in the Chemical Composition and Physical Properties of American Oats. By C. Richardson (*Amer. Chem. J.*, **8**, 364—374; compare Abstr., 1885, 585).—The grains vary considerably in weight, size, weight of husk, and in the way in which the husk encloses the grain, according to the environments of the plants. The chemical composition, however, is far more constant, and the proportion of husk and kernel and the compactness of the grain prove to be the all-important factors, and the weight per bushel the best means of judging of the value of the grain. No differences can be shown to exist such as might be expected between the largest and smallest oats, those having the lowest and highest proportion of kernel, &c. The detailed results are embodied in a series of tables. H. B.

Loss occasioned by Improper Methods of Pickling Wheat. By P. Grassman (*Bied. Centr.*, 1886, 766—774).—It is customary to treat wheat before sowing with solution of copper sulphate, which destroys the spores of bunt (*Tilletia caries*), but generally no special attention is paid to the quantity of sulphate employed; consequently much loss ensues, owing to the destructive action of the sulphate on the germinative power of the grain. Kuhn recommends that for every 5 bushels of wheat 1 lb. of sulphate be dissolved in 50 parts of water. In this solution, the wheat is to be soaked for 12 to 16 hours, after which, the liquid being first removed from above, the grain is to be dried for 24 hours. The liquid is to be removed from above, because the diseased grains and the fungus float to the top, so that if the liquid is drawn off from below, or if the grain is lifted out through the liquid, the damaged grain and spores will be mixed again with the healthy material. Grossman has examined the effect of prolonged drying and increased strength of solution on the vitality of the seed, and finds that both of these conditions are highly detrimental to the germinative power, and that where germination is not actually destroyed, the sprout will be unhealthy and weak, and germination will be delayed. Tables are given showing in detail the results of various mixtures and times of drying on the germination.

E. W. P.

Nitrogen Compounds in Vegetable Soils. By Berthelot and André (*Compt. rend.*, **103**, 1101—1104).—The nitrogen in vegetable soils exists mainly in the form of insoluble compounds with carbon, hydrogen, and oxygen.

Sieved and air-dried soil was suspended in water, mixed with various proportions of hydrochloric acid, kept at different temperatures for varying lengths of time, and then filtered. The filtrate was

carefully neutralised with potash, then slightly acidified, and afterwards mixed with excess of magnesia, and the ammonia estimated by Schloesing's process. The ammonia was also determined in the soil which had been in contact with water only, and the difference between the two quantities gave the amount of ammonia formed by the action of the acid on the nitrogen compounds in the soil. The quantity of ammonia thus formed increases with the concentration of the acid, the time, and the temperature. The action of the hydrochloric acid is in fact precisely similar to its action on urea, asparagine, oxamide, &c. (this vol., p. 235), and hence it follows that the nitrogen in the soil exists in part at least in the form of amides.

After estimation of the ammonia, the liquid was carefully neutralised with sulphuric acid, evaporated to dryness on the water-bath, and the nitrogen in the residue estimated by means of soda-lime. This determination gives the amount of nitrogen present in the form of soluble amido-compounds, and it was found that the proportion of these compounds increases with the time of action of the hydrochloric acid and with its concentration. The amido-compounds thus rendered soluble by the action of the acid may be divided into two groups, one of which remains in solution when the liquid is neutralised with potash, whilst the other is precipitated with the ferric, aluminium and calcium oxides. In one experiment, the ratio between the nitrogen in the two groups was 23 : 17.

Alkalis act on the nitrogenous matter in much the same way as hydrochloric acid. C. H. B.

Manuring Rye with Thomas Slag and other Phosphates. By M. Sievert (*Bied. Centr.*, 1886, 744—745).—The land had been manured in the previous year with farmyard manure, and in this season it received 30 lbs. P_2O_5 and 10·5 lbs. N as ammonium sulphate or bone-meal per morgen. The phosphates applied were Thomas slag, bone-meal superphosphate, and Curaçoa phosphate. In all cases the slag brought the lowest, and the superphosphate the highest yield, and from a money point of view the super- and Curaçoa phosphates were the most advantageous. E. W. P.

Thomas Slag and other Phosphates as Manure for Moorlands. By Rimpau and others (*Bied. Centr.*, 1886, 732—742).—In the previous year, the phosphates failed to produce any definite result (Abstr., 1886, 1069). The experiments have been repeated in the succeeding year without added manures, so as to obtain information regarding the after-effect of the manures. It appears, then, that the after-action of Thomas slag and precipitated phosphate are alike. A set of experiments similar to those already described (*loc. cit.*) have been made by Wagenheim, from which it appears that as a manure for rye, slag is as good as precipitated phosphate; moreover, P. Wagner's law, that so long as an increase is obtained by the employment of increased quantities of phosphate, that increase will be in direct ratio with the increase of manure, was corroborated.

Another corroboration of Wagner's law was also obtained when rye was grown, and a distinct advantage of slag over precipitated phos-

phate was noticed, in that the expenses were less with the former than with the latter. E. W. P.

Superphosphate Manuring for Sugar-beet. By A. Nautier (*Bied. Centr.*, 1886, 742—744).—It was found in the neighbourhood of Peronne, where the land was rich (P_2O_5 0·34 per cent, N. 0·17, K_2O 0·53), that the addition of manures (nitre, ammonia, oil-cake, and phosphate) was unnecessary, as instead of an increase in the crop which paid for the manure the case was exactly opposite; there was a deficiency and loss. Neither was the percentage of sugar in the juice appreciably altered. But, on the other hand, in poor land deficient in phosphates, a gain was obtained by the use of superphosphate and natural phosphates, yet the total yield was lower, although the quotient of purity was higher than on the richer soil.

E. W. P.

Analytical Chemistry.

Filters with Greased Edge. By A. Gawalovski (*Zeit. anal. Chem.*, **26**, 51).—By soaking the edge of a filter with paraffin, wax, or fat (free from ash), the tendency which some precipitates have to creep over the edge is entirely removed. M. J. S.

Method of Estimating Fluorine. By A. Chapman (*Chem. News*, **54**, 287).—The ignited substance is pulverised and repeatedly treated with 10 per cent. hydrochloric acid, the combined extracts are made up to a definite volume, and an aliquot part treated with acid ammonium acetate, which precipitates calcium fluoride; the precipitate is washed, dried, ignited and weighed. As calcium phosphate is not precipitated under these circumstances, the method is well adapted for the analysis of commercial phosphates. D. A. L.

Reagents for detecting Minimal Quantities of Active Oxygen. By C. Wurster (*Ber.*, **19**, 3195—3205).—Tetramethylparaphenylenediamine, $C_6H_4(NMe_2)_2$, is converted by all oxidising agents into a blue-violet dye, only capable of existing as a salt, $C_6H_4<^{NMe_2Cl}_{NMe—}>CH_2$. This, when further oxidised, changes from red-violet to red, and finally becomes colourless. It can be reduced to the original base. Paper soaked with a solution of tetramethylparaphenylenediamine forms a very delicate test for active oxygen. It shows the presence of active oxygen in the air, in the neighbourhood of flames, in the sap of plants, and in the human skin. The moist paper is also coloured by silver oxide and by red-lead. Solution of copper sulphate or the dry salt, spongy platinum, wood charcoal, and many other powders, aldehyde, ethereal oils, some alcohols and acetone colour the paper. It is also coloured by most disinfectants in sunlight, by chlorophyll, and by some ferments.

Chloric and nitric acids do not colour the paper quickly; but when salts of these acids are treated with strong sulphuric acid the gases evolved rapidly oxidise the diamine.

When hydrogen peroxide and tetramethylparaphenylenediamine, both in the purest possible state, are brought together the solution is scarcely coloured; on adding paper or a chip of wood, an intense coloration is produced, which lasts for days. Very dilute nitrite solution (1 : 1000 or 1 : 10000) gives an intense coloration, but is decolorised again almost immediately. Even a solution of a nitrite diluted to 1 : 10,000,000 is slowly decolorised.

Dimethylparaphenylenediamine, when oxidised, yields a fine red dye; this changes to a violet or blue dye when kept, or when heated. When the free base is brought into contact with the skin, the latter is often coloured brown or black in a short time. Paper prepared with the diamine remains blue-violet for two or more hours in a mixture of hydrogen peroxide, and acetic or lactic acids; decolorisation takes place quickly on adding salt to the solution; this is probably due to the liberation of hydrochloric acid.

The oxidation of the methyl-derivatives of phenylenediamine is quantitative, and can be shown by potassium permanganate in hydrochloric acid solution. N. H. M.

Influence of Copper on the Estimation of Sulphur. By W. F. Brugman (*Chem. News*, **54**, 290—291).—The author's experiments indicate that when copper is present in quantities not exceeding 1 per cent. it does not interfere with the working of the "hydrogen sulphide method" of estimating sulphur in iron and steel. There has been much difference of opinion on this point. D. A. L.

Eggerzt's Method of Estimating Sulphur in Iron. By G. Möller (*Chem. Centr.*, 1886, 489—490).—The author has reinvestigated this method, and finds the results to be unsatisfactory.

Estimation of Sulphur in Coal and Coke. By A. J. Atkinson (*J. Soc. Chem. Ind.*, **5**, 154—157).—The author's method is a modification of Nakamura's process of heating pulverised coal in contact with sodium carbonate, whereby the coal rapidly undergoes complete atmospheric oxidation, the combustion of the carbon being effected at a dull red heat over a spirit-lamp (compare Trans., 1879, 785). The difficulty with which the heat from a spirit-lamp can be evenly distributed over the whole of the test, suggested to the author that the combustion could be more easily conducted in a muffle through which a gentle current of air is made to pass. The author has also made a series of experiments with the object of proving the applicability of this method to the estimation of the sulphur contained in pyrites, but the results have hitherto been far from satisfactory. If by some simple device, the complete oxidation of the sulphuric acid could be secured, the amount of this acid might be determined by finding the quantity of standard sulphuric acid required to neutralise the excess of sodium carbonate, and deducting that amount from the quantity

required to neutralise the whole of the sodium carbonate weighed out. D. B.

Estimation of Sulphur and Impurities in Coal-gas. By T. Fairley (*J. Soc. Chem. Ind.*, **5**, 283—286).—The author's process of estimating sulphur in coal-gas consists in using a very dilute solution of hydrogen peroxide, run in at the top of the referees' apparatus, and the plain flame under the trumpet without ammonium carbonate. The oxidising effect is very complete, even with solutions containing less than 1 per cent. of peroxide. The equation is $H_2O_2 + SO_2 = H_2SO_4$, and hence the liquid may either be titrated with standard alkali, or acidified and precipitated with barium chloride. The method may be used either intermittently or continuously. In the former case the sulphuric acid in the condensed liquid and washings may be determined either by titration, or precipitation, or both; and in the latter, the receiver being changed, the volume of gas required is burnt, and then the sulphuric acid is estimated in the liquid collected, without disturbing the rest of the apparatus. The estimations of carbonic anhydride and of ammonia in coal-gas are made by processes substantially the same as those described in text-books. Where the carbonic anhydride is over 1 per cent., approximately accurate results may be obtained by the use of Bunte's gas burette. When the gas has been purified by lime, the carbonic anhydride may fall under 1 per cent., and then a standard solution of barium hydroxide should be used, contained in an ordinary absorption apparatus arranged to give as small bubbles of gas as possible. After passing a measured volume of the gas through a measured quantity of the barium solution, and allowing the precipitated carbonate to settle, a portion of the clear liquid may be titrated. The loss of alkalinity gives the carbonic anhydride present in the gas.

D. B.

New Reaction of Thiosulphates. By L. L. de Koninck (*Zeit. anal. Chem.*, **26**, 26).—A mixture of an alkaline thiosulphate with aqueous potash or soda yields an alkaline sulphide when treated with aluminium. M. J. S.

Detection of Ammonia, Nitric or Nitrous Acids, and Thiosulphuric Acid in a Mixture of Alkaline Salts. By L. L. de Koninck (*Zeit. anal. Chem.*, **26**, 26—27).—Aqueous soda is added, and the mixture boiled in a fractionating flask connected with a U-tube containing Nessler solution. When all the ammonia is expelled, aluminium foil is introduced, and the presence of the nitrogen acids is recognised by testing a second distillate for ammonia. Finally, the tests for a sulphide are applied to the residue in the flask (compare preceding Abstract). M. J. S.

Determination of Ammonia in Arable Soil. By W. Knop (*Zeit. anal. Chem.*, **26**, 1—9; compare Baumann, this vol., p. 82.)—The determination of ammonia in soil by means of hypobromite is complicated by the fact that clay, especially when ferruginous, undergoes contraction when shaken with a strongly alkaline solution. This

contraction is quite unconnected with the absorption of oxygen, which occurs when humus is shaken with air and an alkali. The amount of the contraction is proportional to the quantity of alkali and the time of shaking. The addition of borax prevents it entirely.

A solution prepared as follows, whilst not containing sufficient free alkali to produce this contraction, decomposes ammonia readily. To an excess of calcium hydroxide 200 c.c. of water and 15 c.c. of bromine are added; the mixture is allowed to remain for several days that the solution may become saturated with lime; it is then filtered and mixed with a saturated solution of borax before use. If it is desired to render this solution more strongly alkaline, it is necessary to ascertain first the maximum amount of alkali which can be used without causing contraction. This may be done by shaking the earth with borax solution, and gradually increasing quantities of sodium hydroxide in a flask, closed with a cork, carrying a sealed capillary tube, the point of which is afterwards broken while in connection with the azotometer. The flask should have a thermometer inserted through a tubulus, and proper precautions against change of temperature must be taken. M. J. S.

Griess' Reaction for Nitrous Acid in Presence of Hydrogen Peroxide. By C. Wurster (*Ber.*, **19**, 3206—3208.)—Fresh saliva failed to give Griess' colour reaction for nitrites, but coloured tetramethylparaphenylenediamine paper. This is accounted for by the presence of hydrogen peroxide which would oxidise the nitrite to nitrate, so that the coloration could only take place in presence of an excess of nitrite. The absence of nitric acid in fresh saliva is seen when saliva is added to two portions of metaphenylenediamine sulphate in glacial acetic acid, one of which is previously treated with a drop or two of ammonia; no coloration is produced in the solution free from ammonia, whilst that containing ammonia is soon more or less coloured, owing to the oxidation of the ammonia to nitrous acid by the hydrogen peroxide.

Saliva obtained from a large dog was found to contain much hydrogen peroxide, and to be free from nitrites and potassium thiocyanate. N. H. M.

Apparatus for Kjeldahl's Method of Nitrogen Determination. By H. P. Armsby and F. G. Short (*Amer. Chem. J.*, **8**, 323—326).—The distillation flask is closed by a rubber stopper with three holes. Through one hole passes a tube of half inch diameter, widening upwards to 1 inch, and about 4 inches long; sealed into the side of this is the exit tube, which is connected with a block-tin condenser; the top of the 1-inch wide tube is closed by a rubber stopper, through which passes a stoppered funnel whose stem reaches to the bottom of the flask, the remaining space in the wide tube is filled with glass beads, to stop any spray. The second hole serves for a small mercury valve to admit air in case of sudden absorption or cooling. The third hole carries a syphon tube reaching to the bottom of the flask, this serves to empty and clean the flask after each operation, so that the apparatus is never dismounted. H. B.

Determination of Phosphorus in Iron and Steel. By P. Vorwerk (*Zeit. anal. Chem.*, **26**, 51).—The modified method proposed by Huss (Abstr., 1886, 1073) yields results which are too low; the organic matters dissolved by the nitric acid render the precipitation of the phosphoric acid incomplete, a defect which is not removed by the quarter-hour's boiling, or by the addition of ammonium chloride.

M. J. S.

Determination of Boric Acid. By T. Rosenbladt (*Zeit. anal. Chem.*, **26**, 18—23).—Boric acid can be completely volatilised by repeated distillation with dry methyl alcohol. The substance is placed in a dry flask fitted with a stopcock funnel and condenser. The lower end of the condenser is fitted by a cork into an empty flask, from which a double bent tube dips under ammonium carbonate solution. The substance is moistened with methyl alcohol, then a small excess of concentrated sulphuric acid is added, and a further quantity of methyl alcohol. This is distilled over into the lower flask, as are also several subsequently added quantities: 40 to 50 c.c. of the alcohol in 8 or 10 portions will carry over 0·3 gram of B_2O_3 completely. The distillate is then mixed with ammonium carbonate and evaporated in a platinum basin, in which about 3 parts of magnesia for 1 of boric acid have been strongly ignited and weighed. The increase of weight gives the amount of B_2O_3.

Substances insoluble in acid require to be fused with alkaline carbonates. If containing fluorine, they must first be strongly ignited. If chlorides are present, an excess of silver sulphate must be added before distilling. The methyl alcohol employed must not darken or evolve sulphurous acid when heated with sulphuric acid.

The test determinations communicated are highly satisfactory. (Compare next Abstract.)

M. J. S.

Separation and Estimation of Boric Acid. By F. A. Gooch (*Chem. News*, **55**, 7—10; compare preceding Abstract).—Boric acid is proved experimentally to be more volatile in methyl alcohol than in ethyl alcohol or in water. This volatility is diminished by the presence of water, hydrochloric acid, amyl alcohol or sulphuric acid; but the residue from the treatment of borax with hydrochloric, nitric, or acetic acid parts readily with its boric acid in the vapour of methyl alcohol; in the last case owing to the tendency of sodium acetate to become alkaline, the residue must be kept acid with acetic acid. For the retention of the boric acid thus volatilised, so as to weigh it after an ignition, magnesium oxide proved unsuitable, owing to its insolubility; lime, on the other hand, is quite efficient, but with lime, hydrochloric acid must not be used for decomposing the borate, as the chlorine of calcium chloride is not readily driven off by heat. On these facts the following method is based:—The substance dissolved in water and nitric acid, or acetic acid, or in the acids alone, is run into a retort connected with a condenser and receiver, and heated by means of a paraffin bath and distilled to dryness. The residue is treated six times successively with 10 c.c. of methyl alcohol, being evaporated to dryness after each addition; when nitric acid is used, a little water is added from time to time to break up the cake of

nitrate; when acetic acid has been used, a few drops of acetic acid are added with the fourth portion of methyl alcohol. In all cases the receiver contains a quantity of lime ignited and weighed before and after the distillation; any increase in the latter weighing is due to boric acid. When chlorides are present in the original substance it is best to dissolve it in nitric acid, and remove the chlorine by means of silver nitrate before distilling, although decomposition with acetic acid and direct distillation may be used successfully. The number of distillations required really depends on the quantity of boric acid present. A neat and convenient apparatus is described which may prove useful in other similar operations, besides this for which it was devised. Many experimental details of interest are also included in the original paper. D. A. L.

Absorption Tubes for Estimating the Carbonic Anhydride in Air. By T. C. Van Nüys (*Amer. Chem. J.*, **8**, 315—323; compare Abstr., 1886, 835).—The carbonic anhydride is absorbed in two long tubes shaped like Guy-Lussac burettes, but provided at the bottom with an outlet and stopcock. They are filled with air free from carbonic anhydride, baryta-water is introduced, and the air to be analysed aspirated through; the tubes are then emptied and rinsed into a flask for titration. Full particulars are given of all the precautions necessary. H. B.

Microscopical Analysis. By K. Haushofer (*Jahrb. f. Min.*, 1887, **1**, Ref., 13—15).—A number of substances, when treated with hot, concentrated sulphuric acid in an assay tube (0·2 c.c. of acid to 10 mgrms. of the substance), are oxidised and partially dissolved. On cooling, anhydrous sulphates frequently separate out, the crystalline form of which, detected under the microscope, may be characteristic for certain metals. Thus, *copper* compounds give a green residue, which, under the microscope, is seen to consist of colourless or pale violet hexagonal plates (rhombic ?), the plane angles of which measure 120°. *Iron* compounds give colourless, thin tablets, rhombic in appearance, with an acute plane angle of 87°. *Zinc* compounds give prisms with forked ends, suggesting the forms of gypsum crystals. *Mercury* compounds give a colourless crystalline powder; the crystals rarely have distinct forms; they are tabular crystals with a rhombic character. *Silver* compounds, with the exception of the halogen salts, give rhombic pyramids with an acute basal angle of 77°, and with indications of the planes of a doma, and of vertical pinacoids. Only a few of the *nickel* compounds occurring in nature give salts which crystallise distinctly. Nickel arsenide, gersdorffite, and ullmannite give forms resembling square prisms with a pyramid superimposed. Of the *manganese* compounds, manganese spar and manganese sulphide give rather large prisms with oblique terminal planes. On exposure to the air, a mass of smaller prisms is formed. Manganite, braunite and hausmannite give colourless prismatic crystals. *Arsenic* compounds give octahedra of As_2O_3, in addition to the sulphates. *Antimony* oxide and sulphide give colourless, prismatic crystals. All the *borates* occurring in nature are decomposed in concentrated sulphuric acid. On cooling, the boric acid separates out in

what seem to be hexagonal tablets. This method is not adapted for the detection of boron in tourmaline and axinite. B. H. B.

Microchemical Tests. By K. Haushofer (*Jahrb. f. Min.*, 1887, **1**, Ref., 15—17).—*Tellurium* treated with concentrated sulphuric acid gives an amaranth-red colour. On heating, the red colour disappears, and tellurous anhydride separates out on cooling in colourless, hexagonal tablets. The crystals are soluble in water, and on evaporation separate out again; the tellurous anhydride obtained by evaporation being rhombic.

Selenium dissolves in concentrated sulphuric acid with a leek-green colour, and on cooling gives a brick-red sediment of selenium.

Bismuth treated with boiling, concentrated sulphuric acid gives numerous very small prisms on cooling. On exposure to air, these rapidly dissolve, and acicular crystals grouped in the shape of a star are formed. These also disappear after a short time. After a few hours large, transparent, monoclinic tablets are formed.

Solutions containing 0·1 gram of *barium* chloride in 20 to 80 c.c., treated with 1 c.c. of concentrated hydrochloric acid, give, with dilute sulphuric acid, rectangular crystals which may be distinctly recognised. With *strontium*, very perfect, rhombic crystals are obtained.

On precipitating *lead* from boiling dilute solutions with sulphuric acid, the sulphate appears as sharply defined rhombic tablets. If this precipitate is washed and treated with a drop of hydrochloric acid, the characteristic long lamellæ and rhombic crystals of lead chloride are immediately formed. B. H. B.

Titration of Zinc and Cadmium Sulphides with Iodine. By P. v. Berg (*Zeit. anal. Chem.*, **26**, 23—25).—The filter containing the washed sulphides is thrown, as soon as it is drained, into a bottle which contains about 800 c.c. of recently boiled water, and from which the air has been expelled by carbonic anhydride. The bottle is well shaken to break up the precipitate, otherwise the separated sulphur would partially protect the metallic sulphide. A moderate quantity of hydrochloric acid is added (which need not entirely dissolve the precipitate), and then an excess of iodine solution of known strength. The residual free iodine must, without loss of time, be titrated with thiosulphate. The whole operation takes about five minutes. The results obtained on known quantities ranged from 98·8 to 100·2 per cent. In the case of manganese, only about 95 per cent. was obtained. Cobalt and nickel sulphides are not attacked by the acid iodine solution. M. J. S.

Valuation of Zinc-dust. By F. Weil (*Compt. rend.*, **103**, 1013—1014).—The zinc-dust is mixed with a standard solution of cupric chloride containing 10 grams of metallic copper per litre, and when all the zinc has been dissolved, the liquid is poured off, strongly acidified with hydrochloric acid, and the excess of copper determined by means of a standard solution of stannous chloride (Abstr., 1883, 509).

The copper solution is prepared by dissolving cupric oxide (from

the nitrate) in hydrochloric acid, and then adding ammonia until a very slight turbidity is produced. If the substances are mixed in a platinum dish, solution takes place rapidly. If a porcelain dish is used, a flat spiral of platinum wire must be placed in the liquid. In order to ascertain if all the zinc has been dissolved, the precipitate is touched with a clean platinum wire; if the wire acquires a red or black coating some zinc is still undissolved, but if it remains bright the reaction is complete. C. H. B.

Detection of Mercury in Organic Liquids. By A. Almén (*Arch. Pharm.* [3], **24**, 1031).—This method is a modification of Reinsch's. In the liquid mixed with 8—10 per cent. hydrochloric acid a well-ignited copper or better brass wire is immersed, and the whole is heated gently during $1\frac{1}{2}$ hours. The wire is then white if much mercury is present or dirty grey if less; it is dried on paper, placed in a small glass tube, which is sealed off a few mm. above the wire. On carefully heating so as to distil off the mercury, there appears close to the wire a reddish-brown non-volatile incrustation, then mercury beads, beyond yellow oil drops, and finally a little water. A lens or microscope may be necessary for the examination of the deposits. In the case of urine, a considerable quantity can be heated with aqueous soda, with or without sugar as a reducing agent; after settling, the test can be applied to a portion of the sediment.

J. T.

Separation of Mercury and Palladium from one another, and from Lead, Copper, and Bismuth. By T. Rosenbladt (*Zeit. anal. Chem.*, **26**, 15—18).—The sulphides of mercury and palladium are soluble in potassium thiocarbonate, whilst those of lead, copper, and bismuth are insoluble. A solution prepared by dissolving 1 part of sulphur in 2 parts of carbon bisulphide and adding 23 parts of aqueous potash of sp. gr. 1·13, will dissolve 20 grams of mercuric sulphide per litre.

The mixed sulphides are boiled for half an hour with a sufficient quantity of the thiocarbonate, and the insoluble sulphides are washed until the filtrate is colourless. From the solution, both mercury and palladium may be thrown down by hydrochloric acid, but a stream of carbonic anhydride precipitates the mercury only. The mercuric sulphide contains free sulphur, which, after drying, may be conveniently removed by extraction with carbon bisulphide in a Soxhlet's apparatus.

The results reported leave nothing to be desired as regards accuracy.

M. J. S.

Estimation of Alumina and Iron Oxide in Mineral Phosphates and Manures. By R. T. Thomson (*J. Soc. Chem. Ind.*, **5**, 152—154).—After considering the methods of separating the phosphates of aluminium and iron from acid solutions containing these substances in conjunction with calcium phosphate, the author gives a process for determining these compounds in commercial phosphates. Two or three grams of the substance is dissolved in hydrochloric acid, evaporated to dryness, the residue redissolved in hydrochloric acid, diluted, and filtered. The phosphates are then precipitated

either by ammonium acetate or by neutralisation with ammonia, soda, or potash. In the former case, a large excess of acetic acid should be used to ensure the complete removal of the lime. The precipitate is then collected on a filter and washed repeatedly with cold 1 per cent. solution of ammonium nitrate, containing di-ammonium hydrogen phosphate equivalent to 0·05 gram phosphoric anhydride per litre. It is then thoroughly washed with the same solution (hot), and finally once with water, then dried, ignited, and weighed. It may then be dissolved in hydrochloric acid, reduced with stannous chloride, and the iron determined by standard potassium dichromate. The result is calculated to iron phosphate, which is subtracted from the weight of the precipitate, and the remaining aluminium phosphate calculated to alumina. Test analyses gave good results.

If a high result is apprehended from the precipitation of calcium phosphate, the precipitate may be dissolved in hydrochloric acid, excess of caustic soda added, boiled, and filtered. The iron in the residue is then determined volumetrically; and the alumina in the filtrate, after acidifying with hydrochloric acid, by either of the above methods. It is advisable to add some phosphoric acid or ammonium phosphate to ensure the presence of an excess of the former sufficient to produce normal aluminium phosphate. When the mineral phosphates contain fluorides, it is best to heat the weighed portion of the sample with concentrated sulphuric acid until these compounds are decomposed and all the hydrofluoric acid is expelled. The residue is then treated with hydrochloric acid and the determination proceeded with. D. B.

Estimation of Nickel in Ores, Mattes, Slags, &c. By T. Moore (*Chem. News*, **54**, 300).—After the separation of copper, arsenic, &c., in the usual manner, the strongly acid solution is diluted, and an excess of sodium phosphate added; any precipitate formed is redissolved by the aid of acid. The whole is boiled, and while boiling, sodium acetate is added until all the iron phosphate is precipitated, the boiling is continued for a minute, and the precipitate collected and washed with hot water containing a little sodium acetate and acetic acid. The filtrate is warmed and treated with potash and bromine. The precipitate is dissolved in warm, dilute sulphuric acid, made strongly alkaline with ammonia, and electrolysed. Metallic nickel is deposited, the small quantity of iron present which has escaped precipitation floats about as an insoluble oxide, and does not influence the results, whilst chromium and manganese remain in solution; part of the latter is deposited on the anode as peroxide (compare Abstr., 1886, 921). The aluminium remains with the iron. When greater accuracy is required, the precipitation of the iron may be repeated. D. A. L.

Volumetric Determination of Chromium. By W. J. Sell (*Chem. News*, **54**, 299—300).—The author has devised a method of applying to analytical purposes the reaction between hydrogen peroxide and chromium oxides (see Martinon, Abstr., 1886, 984). The aqueous solution of the substance to be analysed is treated with sufficient potash to dissolve the precipitate first formed, hydrogen

peroxide is then added, and the whole boiled briskly for at least 15 minutes, the chromic acid is then easily determined by any method in the resulting solution of the chromate formed. Aluminium and zinc do not interfere with the reaction, but with iron the results are low. The method was devised before the publication of the paper referred to. Another use for hydrogen peroxide is suggested for qualitative purposes. The ammonium precipitate in group III is dissolved in dilute nitric acid, poured into excess of potash containing hydrogen peroxide, boiled and filtered. The solution contains the aluminium and the chromium as chromate; the iron, &c., being precipitated.

D. A. L.

Analysis of Chrome Paints. By W. L. Brown (*Chem. News*, **54**, 329—331).—Mixtures of lead chromate and sulphate, or chromate, sulphate and carbonate, are treated with hydrochloric acid for insoluble adulterants, whilst the solution is used for the chromium and sulphuric acid determinations. For lead, the paint is decomposed with concentrated sulphuric acid, and the lead, as in all succeeding cases, is weighed as sulphate. Red chromate of lead is decomposed with nitric acid and a few drops of alcohol added to facilitate the solution of the chromium. Chrome-green is treated with hydrochloric acid; lead, chromium, sulphuric acid, and sometimes iron, pass into solution, the Prussian blue, &c., remains as residue (it is sometimes slightly attacked). Any lead found in excess of that required by the chromium and sulphuric acid, is regarded as carbonate. Full details of separation, &c., are given in the paper. D. A. L.

Estimate of Chromate in the Presence of Dichromate. By N. McCulloch (*Chem. News*, **55**, 2—3). As is well known, the blue coloration soluble in ether which results from the action of hydrogen peroxide on chromic acid is only produced with dichromates in acidified solutions, or with chromates to which acid has been added in excess of that required to convert them into dichromates. The following quick and ready method for estimating chromate in the presence of dichromate is founded on this basis. The substance, dissolved in a little water, is mixed with a few c.c. of hydrogen peroxide solution and covered with a layer of ether, standard sulphuric acid is run in gradually until after agitation the ether assumes a blue colour. From the quantity of acid used, the amount of chromate present is easily calculated. D. A. L.

Estimation of Tin and Lead in Alloys. By O. Wachsmuth (*Chem. Centr.*, 1886, 491).—For the rapid estimation of the composition of alloys of these two metals, the author recommends the determination of the specific gravities and melting points.

The specific gravities are not sensibly affected by the small admixture of antimony (2 to 5 per cent.), used in preparing many alloys. The specific gravities and melting points of mixtures of tin and lead, containing from 5 to 95 per cent. of each metal, are given.

C. F. C.

Colour Reactions of Titanic, Niobic, Tantalic, and Stannic Anhydrides. By L. Levy (*Compt. rend.*, **103**, 1074—1076).—

various colour reactions given by these anhydrides with certain alkaloïds, phenols, and with hydroxybenzoic acids in presence of concentrated sulphuric acid are described. The colours disappear when water is added, except in the case of stannic anhydride, and the substances must be free from nitrates and nitrites. Silica, alumina, and zinc and uranium oxides give no similar colour reactions.

In order to detect the four anhydrides when mixed together, the substance is strongly heated with ammonium carbonate to remove nitrites and nitrates. Different portions are then mixed with strong sulphuric acid and one of the following reagents: morphine, a crimson colour indicates titanic anhydride; codeïne, a mauve colour indicates niobic anhydride; resorcinol, an amethyst colour, tantalic anhydride (green if much titanic and niobic anhydrides are present); α-naphthol and a few drops of water, amethyst colour, stannic anhydride.

These reactions may be used in the reverse way to detect certain alkaloïds and phenols. C. H. B.

Colour Reactions of Arsenic, Arsenious, Vanadic, and Molybdic Anhydrides, and of Antimony and Bismuth Oxides. By L. Levy (*Compt. rend.*, **103**, 1195—1196).—A continuation of the author's previous experiments (preceding Abstract). In most cases the colours are destroyed or modified by the addition of water.

Arsenic anhydride mixed with catechol gives a grey-green colour, which changes to amethyst. In this way it can be distinguished from phosphoric anhydride, which gives no coloration, and from vanadic anhydride, which gives a dark green colour, becoming paler on addition of water. With arsenic anhydride, resorcinol and quinol give respectively a sepia and a yellowish coloration, and it is evident therefore that this reaction may be used to distinguish between these three isomeric dihydric phenols.

Vanadic anhydride with resorcinol gives a dark green coloration, which becomes violet on addition of water, and it can be distinguished by this reaction from molybdic and phosphoric anhydrides.

Bismuth oxide and catechol give a greenish coloration, which becomes deeper after the addition of water. Antimony oxide and arsenic anhydride give a flesh coloration under the same conditions.

Arsenites give a flesh tint with catechol, which distinguishes them from the arsenates, whilst α-naphthol gives no coloration with any of the oxides similar to that which it gives with stannic oxide.

C. H. B.

Post-mortem Detection of Chloroform. By C. Luedeking (*Amer. Chem. J.*, **8**, 358—361).—The lungs or other viscera are made slightly alkaline by sodium carbonate, and heated on a water-bath in a flask, through which a current of air is passing. The escaping gases are passed through a short length of red-hot tube, and then tested with potassium iodide and starch paper. As the result of six experiments on dogs it is shown that chloroform may be detected at least four weeks after death, even when the carcases have been exposed to the air at full summer's heat; during the decomposition no substances are formed which interfere with the above tests. H. B.

Estimation of Glycerol in Wine and Beer. By SKALWEIT (*Chem. Centr.*, 1886, 541).—The author isolates the glycerol in the usual way, obtaining it in a concentrated form, in which, the aggregate weight having been determined, the percentage of glycerol is estimated by determining the coefficient of refraction in the Abbé instrument. Full details are given. C. F. C.

Separation and Quantitative Estimation of Melitose (Raffinose) in Cane-sugar. By C. SCHEIBLER (*Ber.*, **19**, 2868—2874. Compare Abstr., 1885, 962.)—Further evidence has confirmed the formula $C_{18}H_{32}O_{16} + 5H_2O$ for melitose. The best method of drying melitose is to place it in a Liebig's drying tube, heated at 70—80° in a water-bath, and so arranged that a small quantity of air, dried over sulphuric acid, enters it by a capillary tube, whilst a partial vacuum is maintained by a Bunsen pump. After one hour's drying under these conditions, so much water is removed that on raising the temperature of the bath to 100° to complete the dehydration, fusion does not occur. Melitose dried in this way melts at 118—119°; it is very hygroscopic, and in a moist atmosphere gradually absorbs the whole of the water removed by drying.

The author finds that melitose is far more soluble than cane-sugar in commercial absolute methyl alcohol, 100 c.c. of the alcohol dissolving 9·5 and 0·4 grams respectively at the ordinary temperature; on this property is based a method for its extraction from the molasses of beetroot sugar. The crystalline product, dried as described, is extracted with absolute methyl alcohol, and the syrupy residue obtained on distilling off the alcohol, is taken up with a little water, and purified by precipitation with ethyl alcohol.

A method for the quantitative estimation of melitose in cane-sugar has been devised, and is under investigation. According to the details given in the paper, commercial absolute methyl alcohol is saturated with cane-sugar at a known temperature, and the rotatory power of the solution is determined. A known weight of the impure cane-sugar, dried by the above method, is then extracted by 100 c.c. of the solution, the temperature being kept constant, and the rotatory power is again determined. From the increase in the rotation, the amount of melitose present can be calculated. W. P. W.

Quantitative Estimation of Raffinose or Melitose. By R. CREYDT (*Ber.*, **19**, 3115—3119).—Raffinose can be determined either optically or gravimetrically after conversion into mucic acid. In the optical examination of cane-sugar and of raffinose, the amount is calculated by the subjoined formulæ—

$$Z = \frac{C - 0{\cdot}493A}{0{\cdot}827} \qquad R = \frac{A - Z}{1{\cdot}57},$$

in which A = the amount of direct polarisation, B = the polarisation at 20° after inversion, C = the difference between B and A, Z = the percentage of cane-sugar, and R = the percentage of raffinose. This method is, however, not available in the presence of other optically active substances such as dextran or invert sugar. When these are

present, raffinose is best estimated by converting it into mucic acid by the following process:—

About 5 grams of dry substance is treated with 6·0 c.c. of nitric acid, sp. gr. 1·15, and the mixture evaporated to about one-third of its volume on the water-bath. After cooling, a known quantity of water is added, and the separation of the mucic acid assisted by the addition of a known weight of that acid, the whole being well stirred. The precipitate is then collected on a tared filter, dried, and weighed. The weight of the raffinose must be estimated from that of the mucic acid by aid of an empirical table which has been worked out by the author, but is not given in the paper. A. J. G.

Detection and Determination of Lactic Acid. By R. Palm (*Zeit. anal. Chem.*, **26**, 33—35).—Lactic acid, when mixed with lead acetate and alcoholic ammonia, gives a heavy, granular precipitate of the constant formula $3PbO,2C_3H_6O_3$. To examine an animal or vegetable organ for free lactic acid, it is extracted with ether (if for a lactate, acidification with sulphuric acid precedes the extraction with ether), the ethereal solution is evaporated to a syrup, and this is treated with water. The filtered aqueous solution is mixed with lead acetate, and any precipitate produced is filtered off. On adding more lead acetate to the filtrate and then alcoholic ammonia, the lactate is thrown down free from foreign substances. It may be washed with alcohol, in which it is absolutely insoluble, and the amount of lactic acid in it may be ascertained from the loss on ignition. Minute traces of lactic acid may be thrown down with greater certainty by shaking the solution (prepared as above) with an excess of freshly precipitated lead hydroxide. The precipitate produced in either way yields pure lactic acid when decomposed by hydrogen sulphide and extracted with ether. M. J. S.

Use of Turmeric as an Indicator for Citric Acid. By F. Watts (*J. Soc. Chem. Ind.*, **5**, 214—215).—When litmus is employed as an indicator in the determination of citric acid by alkalimetry, the results obtained are frequently too low, on account of the want of sharpness in the reaction. Warington (this Journal, 1875, 925) recommends the preparation of a special litmus-paper, but even with this precaution the difficulty is not entirely removed. The author has obtained good results by using tincture of turmeric in place of litmus. Drops of this tincture are placed on a white tile, the liquid spreading out in bright yellow films. The slightest excess of alkali causes the development of the well-known red-brown colour. In using this indicator, much time is saved by employing litmus-paper to determine the near approach to neutralisation, proceeding with the addition of alkali until the litmus-paper is turned slightly blue, and determining the exact point of neutrality by means of the turmeric. D. B.

Determination of the Fatty Acids in Soap. By B. Schulze (*Zeit. anal. Chem.*, **26**, 27—28).—The soap is decomposed in a conical flask by dilute sulphuric acid. Ether is added to dissolve the fatty acids. The aqueous layer is then removed by a pipette. Water is

added, and is removed in the same way four times. A drop of barium chloride throws down any traces of sulphuric acid still left. The ethereal solution can then be poured off alone on to a filter, and the determination completed as usual. M. J. S.

New Method of Estimating Fat in Milk. By A. Cronander (*Bied. Centr.*, 1886, 706—707).—By the new process, the fat in 40 samples can be estimated in six hours. 100 c.c. of milk is mixed and shaken up for an hour with 10 c.c. of aqueous potash (100 grams KHO in 500 c.c. H_2O) and 30 c.c. of moist ether. After ½ to 1 hour, the ether will have dissolved out all the fat; the several ethereal solutions may then be simultaneously evaporated on a specially constructed water-bath at 60—65°, and finally heated at 80° for ½ hour. To measure the volume of the fat, the flasks containing the fat are fitted with corks, through which pass two tubes, of which the one graduated to fractions of cubic centimetres passes only just through the cork; the other passes nearly to the bottom of the flask. Water is then passed into the flask by the longer tube, so that the layer of fat rises and fills the graduated tube, where it is measured. This measurement gives volume per cent., from which the weight per cent. is calculated, according to the following table:—

Vol. p. c.	Wt. p. c.	Vol. p. c.	Wt. p. c.
1·0	0·89	2·5	2·22
1·5	1·34	3·0	2·67
2·0	1·78	3·5	3·12

The results are fairly accurate, but as the measurement is made at 35°, the percentage is slightly low (0·01—0·05 per cent.).

E. W. P.

Butter Testing. By J. Skalweit (*Analyst*, **11**, 90—91).—It is suggested to employ dialysis in butter testing, inasmuch as the glycerides of the soluble butter acids dialyse much more quickly than the other glycerides contained in butter. The examination of the purified fat in an Abbe's refractometer is recommended as especially worthy of attention. The following tables gives the angles obtained by examining various fats at 20°, water = 1·333:—

Butter olein		1·4635
Olein from commercial oleic acid		1·4635
Oleic acid		1·4639
Genuine Gloucester butter (mean of two experiments)		1·4655
Cocoa butter		1·4680
Lard		1·4690
Butterine, Hanoverian (four experiments)		1·4693—1·4712
Butterine, English		1·4733
Cotton-seed oil	refined	1·4748
	crude	1·4732
Cod-liver oil		1·4801
Linseed oil		1·4835
Margarine oil		1·4680
Margarine, 1st quality		1·4692

D. A. L.

Butter Testing. By H. Hager (*Chem. Centr.*, 1886, 495).—The author recommends the Reichert-Meissl method of examining butter, the chief feature of which is a determination of the volatile fatty acids. The method is simpler and more expeditious than Hehner's. The butter is filtered and 5 grams are saponified with pure sodium hydroxide (2 grams) in presence of alcohol (80 per cent.). The volatile fatty acids are separated by decomposition with sulphuric acid and distillation, and estimated by titrating the distillate with decinormal alkali. The following table gives the number of c.c. of the latter required to neutralise the distillate in the case of certain typical fats:—

Normal butter	26 to 31 c.c.
Oleomargarine	1·9 ,,
Cocoa butter	7·4 ,,
Pig's fat	0·6 ,,

C. F. C.

Butter Analysis. By F. W. A. Woll (*Zeit. anal. Chem.*, **26**, 28—33).—To ascertain the degree of accuracy with which the percentage of true butter in butterine could be determined by Köttstorfer's and Reichert's methods respectively, the author made mixtures of "oleo-oil" and genuine butter, containing 20, 40, 50, 60, and 80 per cent. of the latter, and analysed each mixture by both methods. The genuine butter employed being one requiring a low percentage of alkali (222·2—223·2 mgrms. per gram), the use of Köttstorfer's mean value, 227, indicated in all cases too low a percentage of real butter, the maximum error being 16·1, and the average error 6·5 per cent. Reichert's method (employing the mean factor 7·3) gave much closer numbers (maximum error 4·5 per cent.). (See Abstr., 1879, 406, 983.)

A low specific gravity is a valuable indication of adulteration, most of the materials used in making butterine having a sp. gr. below 0·90536, whilst that of genuine butter is generally between 0·914 and 0·912.

The results of the examination of 37 samples of butter, butterine, and butterine materials are given. M. J. S.

Reichert's Method of Butter Analysis. By H. B. Cornwall and S. Wallace (*Chem. News*, **54**, 315—316).—Reichert's method is very highly recommended. The authors recognise the fact that the proportion of volatile fatty acid varies considerably in different pure butters, and are therefore of opinion that the products of single cows only should be taken into consideration when establishing standards. From this standpoint and from numerous observations, they consider that the minimum standard should not exceed 11 c.c. of decinormal alkali consumed in Reichert's method when 2·5 grams of fat are employed. Moreover, they note that there is no apparent connection between the number of c.c. of decinormal alkali used and any of the following conditions: season of the year, breed, food, age of cow, or time after calving.

The authors' average was 13·68 c.c. decinormal alkali. These results and conclusions differ from those obtained by Munier (Abstr., 1883, 247). D. A. L.

Carrot Colour in Butter. By R. W. Moore (*Analyst*, **11**, 163—164).—When fat coloured with carrot is dissolved in carbon bisulphide and mixed with alcohol, two layers form, the carbon bisulphide solution being yellow, the alcoholic colourless. On adding a drop of dilute ferric chloride, insufficient in itself to colour the alcohol, the carbon bisulphide becomes gradually decolorised, whilst the alcohol becomes distinctly yellow. Beef fat, mutton fat, olive oil, lard, and butter coloured with carrot all respond to this test. Natural uncoloured butter is not decolorised in this manner. D. A. L.

A New Ureometer. By J. Marshall (*Zeit. physiol. Chem.*, **11**, 179—180).—A new apparatus for the estimation of urea by means of the sodium hypobromite method is described and figured. It is a modification of that devised by Greene, the chief difference being that the graduated tube can be easily removed and cleaned.

W. D. H.

Separation of Nitrogenous Substances by Means of Phosphomolybdic Acid. By A. Hirschler (*Zeit. physiol. Chem.*, **11**, 25—40).—Phosphomolybdic acid precipitates proteïds, peptones, gelatin, xanthine, guanine, hypoxanthine, adenine, and creatinine. It does not precipitate aspartic acid, leucine, glycocine, urea, or creatine. In order to make quantitative analyses of nitrogen by Kjeldahl's method, it is not necessary that the phosphomolybdic acid should be first removed if excess has been employed. Proteïd, peptone, and propeptone are, moreover, completely precipitated by this reagent; this precipitate does not carry down with it any leucine or other substances which are not usually precipitated by the acid.

Applying this method for the detection and estimation of leucine in peptic digestion, the teaching of Hoppe-Seyler is confirmed, namely, that a small amount of leucine is formed from proteïd during that process, but much more slowly than in pancreatic digestion.

In experiments on the composition of the liver of animals (dogs) poisoned by phosphorus, it was found that in certain cases of typical phosphorus poisoning, the formation of amido-acids either does not take place at all, or only to a very slight extent. W. D. H.

Opium Testing. By E. Dietrich (*Arch. Pharm.* [3], **24**, 1023—1024).—6 grams of air-dried opium powder is macerated with 60 c.c. of water with occasional shaking during 12 hours and then filtered; 50 c.c. of the filtrate is treated with 2 c.c. of normal ammonia, well mixed and immediately filtered through a ribbed filter. 44·2 c.c. of the filtrate, = 4 grams of opium, is placed in a tared Erlenmeyer's flask with 10 c.c. of ether and agitated with a swinging motion for a minute; 4 c.c. of normal ammonia is now added, well mixed by swinging, and

the flask allowed to remain six hours. The ether layer is now carefully passed through an 8 cm. filter; 10 c.c. of ether is added to the flask, shaken for a moment, and also passed through the filter. The crystals adhering to the flask are washed down by means of the aqueous solution in the flask, which is passed through the filter; the flask and filter are then twice washed with 5 c.c. of water saturated with ether. After well draining both filter and flask, they are dried at 100°, and the contents of the filter are brushed into the flask, which is dried and weighed until constant. In the case of opium extract, 3 grams is taken, dissolved in 42 c.c. of water, allowed to remain for an hour, treated with 2 c.c. of normal ammonia and filtered; 31·7 c.c. of the filtrate (= 2 grams of extract) is treated as above with 10 c.c. of ether and 4 c.c. of normal ammonia. In the case of *Tinctura opii* and *Tinctura opii crocata*, 50 grams of either is evaporated to one-half, the original weight made up with water, 2 c.c. of normal ammonia added, and filtered; 44·2 c.c. of the filtrate is treated as above. The method requires little time, is easily carried out, gives a sharp separation of the various constituents, gives very uniform results, and yields almost the whole of the morphine. J. T.

Microchemical Detection of Tannin. By J. W. Moll (*Ann. Agronom.*, **12**, 496).—Portions of the plant cut into small pieces are placed in a saturated solution of copper acetate (7 per cent.) and allowed to remain for 7—10 days. Sections are made and placed in a drop of acetate of iron of 0·5 per cent. strength for a few minutes, they are then washed with water and transferred to a glass containing alcohol in order to expel the air and to dissolve out the chlorophyll, afterwards they are placed in glycerol for observation. The tannin is precipitated by the copper acetate, and the precipitate is stained green or blue by the iron salt, so that these two classes of tannins can be readily distinguished. J. M. H. M.

Tannin Determination. By E. B. (*Zeit. anal. Chem.*, **25**, 527—528).—The author having been unable to obtain the hide powder required for v. Schröder's method, has employed a solution of ferric acetate, which, when added in excess, throws down all the tannin and gives a clear filtrate fit for titration with permanganate in the usual way. The solution contained 48·2 grams of iron alum, 25 grams of sodium acetate, and 40 c.c. of 50 per cent. acetic acid in a litre. He requests chemists who are in the habit of using hide powder to make comparative determinations with this precipitant. M. J. S.

Thalleïoquinine Reaction. By E. Mylius (*Chem. Centr.*, 1886, 602—603).—About 0·01 gram of the salt to be tested for quinine is treated on a watch-glass with about the same bulk of potassium chlorate and a drop of strong sulphuric acid; ammonia is then added in excess, and the whole stirred, when the solution assumes a dark-green colour. Less than a milligram of quinine can be easily detected by this reaction. L. T. T.

Analysis of Pepper. By C. Heisch (*Analyst*, **11**, 186—190).—It is noted that sand, &c., should be regarded as an adulterant of ground pepper, since almost all sand is removed when the peppercorns are properly cleansed before grinding. The organic matter of pepper should consist of not less than 50 per cent. of starch, which is easily distinguished under the microscope owing to the smallness of the grains; long-pepper starch-grains are, however, very similar to rice starch, but as long-pepper costs nearly as much as good black pepper, it would scarcely be used as an adulterant, and rice with its large proportion of starch could not well be mistaken for pepper. Results of several analyses of pepper are given, including water, ash, starch, alcoholic extract, piperine, &c.; the starch being estimated by boiling with 10 per cent. hydrochloric acid for three hours and polarising. (With regard to the last point, compare Harvey, this vol., p. 125.)

D. A. L.

Hæmatoscopy; a new Method of Blood Analysis. By Hénocque (*Compt. rend.*, **103**, 817—820).—The *hæmatoscope* is a small, wedge-shaped glass cell on which is etched a millimetre scale, by means of which the thickness of the layer of liquid at any point is ascertained. The blood to be examined is placed without dilution in the hæmatoscope, and the thickness of the layer which shows both absorption-bands of equal intensity is determined. The percentage of oxyhæmoglobin is then ascertained from special tables.

The *time of reduction* of oxyhæmoglobin is determined by examining the spectrum of the blood under the thumb-nail. With a direct vision spectroscope the first and sometimes the second band of oxyhæmoglobin can readily be seen. If a ligature is tied round the phalanx, the bands gradually disappear, and the time required for their disappearance after the ligature is tied, is called the time of reduction. This time varies from 25—90 seconds, the mean duration for a healthy person in a state of repose being 60 seconds.

Activity of reduction is measured in the following manner. In a healthy man, with blood containing about 14 per cent. of oxyhæmoglobin, the time of reduction is 70 seconds, from which it is calculated that 0·2 per cent. of oxyhæmoglobin is reduced per second. This quantity is taken as the unit activity of reduction, and the activity corresponding with various times of reduction and percentage of oxyhæmoglobin as determined by the methods just described is obtained by means of the expression—

$$\text{Activity of reduction } \epsilon = \frac{\text{quantity of oxyhæmoglobin}}{\text{time of reduction}} \times 5.$$

C. H. B.

General and Physical Chemistry.

Distinction between Spectral Lines of Solar and Terrestrial Origin. By M. A. Cornu (*Phil. Mag.*, **22**, 458—463).—The dark lines of the solar spectrum are of two kinds. Those of one class (C, F, D, E, G, H, and the magnesium band *b* in the green) are of solar origin, and always present the same aspect: others (A, B, and band *a* in the red) are telluric, produced by selective absorption in the earth's atmosphere, and become broader and darker as the sun sinks towards the horizon. It is by this latter characteristic that they have been chiefly recognised hitherto.

The author's method of distinction is based on Fizeau's principle of the displacement of lines in the spectrum, when the source of light is in a state of absolute or relative motion. This displacement may be connected with the velocity by very simple expressions, and has been used to calculate the velocity of the source. In practice, the method consists in allowing the light from opposite edges of the solar disc (where of course the motions are opposed) to fall on the slit of the spectroscope; the telluric lines remain steady, while the solar lines appear to move. The motion is easily detected by noting the position of any line with respect to one of the particles of dust always found on the cross-wires. It becomes still more sensible when, by an arrangement which is figured and described, the collecting lens is caused to oscillate two or three times a second, so as to throw opposite edges of the sun's image alternately upon the slit. The solar lines are then distinguished at a glance.

The method has been applied to the anatomy of band *a*, and to ascertaining the telluric origin of some lines beyond *δ*, and the solar origin of Kirchhoff's line 1474. Since this line oscillates, the vapour producing it must be carried round by the sun's rotation.

Ch. B.

Spectrum of Germanium. By G. Kobb (*Ann. Phys. Chem.* [2], **29**, 670—671).—The author has examined the spectrum of germanium by viewing in a six-prism spectroscope the spark of an induction-coil taken between terminals of platinum and germanium. The

Wave-length.	Remarks.	Wave-length.	Remarks.
6336·0	—	5131·0	Bright, diffused.
6020·0	very sharp	4813·0	Ditto.
5892·0	ditto	4742·0	Ditto.
5255·5	—	4684·5	Sharp, faint.
5228·5	—	4291·0	Faint, diffused.
5209·0	—	4260·5	Ditto.
5177·5	bright, diffused	4225·5	—
5134·0	—	4178·0	Ditto.

position of each line was determined by micrometric measurements of its distance from two neighbouring solar lines. The results are contained in the table (p. 313), in which wave-lengths are given in $\frac{1}{10^{10}}$ metre. A. H. F.

Fluorescence of the Pigments of Fungi. By A. Weiss (*Chem. Centr.*, 1886, 670—671).—The fluorescence of alcoholic extracts of fungi was examined by means of a cone of light. All gave a greater or less fluorescence, which was green with yellow or brown-coloured fungi, and blue with red or violet-coloured fungi. The ochre-yellow colouring matters of some Agaricinæ give, however, a sky-blue, and the red colouring matter of the heads of *Ammanita muscaria*, a green fluorescence. The spectrum of the blue fluorescent colouring matters of *Russula* shows a wide, very characteristic, black absorption-band in the green and yellow, a feeble one between the lines E and F, and a total absorption of the violet to the line G. The green-yellow band agrees in position with the band which is seen in the spectrum of a living red peony leaf, and also with that given by the blue colouring matter of many Campanulæ, after treatment with sulphuric acid. The more intense the colour of the extract, the more the absorption extends towards the red, so that with a thick layer of liquid the whole of the green and yellow is absorbed. The absorption in the violet is similar to that given by the red, blue, and violet leaf colouring matters of the Phanerogamæ. The green fluorescent colouring matters of fungi show a feeble absorption-band between E and F, and a wide absorption of the violet end of the spectrum, sometimes even the entire end of the spectrum as far as *b* is absorbed. G. H. M.

New Secondary Element. By M. Kalischer (*Phil. Mag.*, **21**, 164).—The element consists of iron (or carbon) and amalgamated lead in contact with mercury, in a solution of lead nitrate. When charged, the iron (as anode) becomes passive and coated with lead peroxide, which protects it from the liquid. During discharge the peroxide is reduced. Electromotive force on open circuit = 2 to 2·5 volts; on closed circuit = 1·8 volts, falling slightly after a time. The lead plate must be occasionally renewed. Ch. B.

Electromotive Force of a Constant Voltaic Cell with Moving Plates. By A. P. Laurie (*Phil. Mag.*, **21**, 409—415).—Before accepting measurements of electromotive force it must be shown, by analysis of the products found in the cell, to what reactions it is really due. This can only be done when the current is passed for a long time, since the electromotive force observed by an electrometer, or by connecting for a short time through a high-resistance galvanometer, may be really due to impurities in the metal, or to a film of gas or oxide on its surface. Hence may arise the want of agreement in some cases between the electromotive forces observed by Wright and those calculated by him from the thermal data.

It is well known that the fall in electromotive force of a cell when the circuit is closed, due to alterations in the layers of liquid in con-

tact with the plates, may be prevented by keeping the liquid in motion. The author has measured the electromotive force of cadmium and platinum immersed in iodine solution, by means of a galvanometer, and finds that it remains constant for a long time when the cadmium plate is kept moving by clockwork. Its initial value was 1·084 volts (by the electrometer 1·076 volts). After two hours, it fell to 1·067 volts (by the electrometer 1·072 volts).

CH. B.

Electromotive Force of Voltaic Cells having an Aluminium Plate as Electrode. By A. P. LAURIE (*Phil. Mag.*, **22**, 213—216).—Wright (Abstr., 1885, 721) has found that the electromotive force (0·538 volt) of zinc-aluminium cells (zinc in zinc sulphate, aluminium in potash alum) is opposite in direction to that calculated from the thermal data (0·938 volt); so also for other aluminium cells. The author attributes these contradictory results to the well-known property of aluminium in contact with air or water of becoming coated with oxide; and states that the abnormal electromotive force (measured by an electrometer) is reduced to 0·14 volt on cleaning the aluminium with sand-paper. When the aluminium plate is amalgamated, the electromotive force becomes *normal*, and equal to 0·46 volt; and the plate is speedily covered with a growth of oxide. Two aluminium wires, one cleaned, the other amalgamated, placed in a solution of aluminium sulphate, give an electromotive force = 1·08 volts.

Wright in reality measured the electromotive force between aluminium oxide on an aluminium plate and zinc; and the value obtained was probably due to the heat of formation of zinc sulphate—that of aluminium sulphate + that of aluminium oxide − that of water.

CH. B.

Electrical Resistance of Soft Carbon under Pressure. By T. C. MENDENHALL (*Phil. Mag.*, **22**, 358—363).—The author describes experiments on this much disputed point, which prove, in his opinion, that a decided diminution occurs in the resistance of carbon when it is submitted to pressure, independently of any change in surface-contact between the carbon and the electrodes through which the current is introduced. For hard carbon, the change is slight, but greater that can be accounted for by any heating effect.

A disc of soft carbon, such as that used in Edison's tasimeter, showed a very great diminution in resistance when compressed between two columns of mercury. A pressure of 5 mm. of water caused a decided deflection in a sensitive galvanometer in circuit; and a pressure of 50 mm. of mercury reduced the resistance to one-half. If the initial pressure was considerable, the disc only slowly recovered its normal resistance after its removal.

Since hard carbon is much more porous than soft, the change should have been less with the latter than with the former, were the action entirely at the surface.

CH. B.

Electrolysis of Silver and of Copper, and the Application of Electrolysis to the Standardising of Electric Current and

Potential Meters. By T. Gray (*Phil. Mag.*, **22**, 389—414).—This paper is chiefly of physical importance. The following points are, however, of general interest.

When the highest accuracy is required in electrochemical measurements, silver solutions are to be preferred to copper solutions; for although silver obtained by electrolysis is apt to be less coherent and less easy to manipulate than copper, it is not liable to oxidation and corrosion by the liquid. In ordinary measurements, however, copper is preferable.

In all cases thorough cleaning of the plates is of supreme importance; the best methods of effecting this are described at considerable length.

The size of the plates may vary within moderate limits for silver, and within wide limits for copper, without affecting the quality of the deposit, and rendering the processes of washing and weighing more difficult. For silver electrolysis, the author recommends a 5 per cent., or at most 10 per cent., solution of silver nitrate, and a cathode plate of not less than 200, nor more than 600 sq. cm. of surface per ampère of current. When the cathode is too small, the deposited metal is not adherent, and tends to grow out in crystals, especially from any sharp edge or corner. An anode plate slightly larger than the cathode is recommended; it should have a surface of at least 400 sq. cm. per ampère. Very small anode plates become black and spongy, and gas is evolved from the surface; but when the plates are large they remain bright, and may be weighed as a check on the weight of the cathode. When a silver anode has not been properly cleaned, the outer layer of metal is not dissolved, but remains as a loose skin. Between successive experiments, silver plates should be heated to redness in a spirit flame.

For the electrolysis of copper sulphate, the cathode plate should have a surface of at least 20 sq. cm. per ampère for short experiments, or 50 for experiments lasting some hours. The anode should expose at least 40 sq. cm. of surface per ampère; but the minimum size depends greatly on the degree of saturation of the copper solution. When this plate is too small, the passage of the current may be completely stopped after a time, owing to the metal becoming coated either with finely crystalline copper sulphate or with oxide. The loss from the anode never exactly equals the gain of the cathode; but when the current density does not exceed $\frac{1}{200}$th of an ampère per sq. cm., the anode may be weighed as a control. It never becomes black and inelastic like a silver anode; in other respects the two behave in a similar way.

The density of the copper sulphate solution may vary between 1·05 and 1·18. With weak solutions, the deposited copper is not very coherent.

A source of error in using copper lies in its corrosion by the liquid. This error is always trifling, and is a minimum for densities between 1·1 and 1·15. Copper plates are more readily corroded by neutral sulphate of copper solution than by a solution containing even 5 per cent. of sulphuric acid; and the action appears to be greater in a cell when the current is flowing that when it is not. A plate of copper immersed in pure sulphate solution at first loses weight by corrosion;

after a time it increases in weight owing to oxidation, and the increase finally becomes rapid owing to the formation of hydrated oxide.

The author gives 0·0003287 gram as the true amount of copper deposited by one coulomb of electricity. But for simple measurements of current the value may be taken as 0·000329 when the cathode has a surface of 50 sq. cm. For other sizes, this number may be corrected by means of a curve which is given. Direct determinations of the constant for silver were not very successful; but they seem to confirm the results obtained by Kohlrausch and by Lord Rayleigh.

Ch. B.

Electrolytic Polarisation produced by Small Electromotive Forces. By C. Fromme (*Ann. Phys. Chem.* [2], **29**, 497—544).—The polarisation of platinum plates in dilute sulphuric acid was measured during the flow of the polarising current, which was always so small as to produce no visible evolution of gases. Two forms of electrolytic cell were employed, the first open, containing two platinum electrodes in cells, joined by a tube containing a third, and a second form in which there were four equidistant electrodes contained in a glass tube. The acid employed varied in strength from 1 per cent. to 3 per cent., the amount of dilution not being found to produce any observable result. With the latter form of cell, the two middle electrodes were joined to the battery through a variable resistance, the two outer plates being for the purpose of measuring the potentials of the others by connection with a quadrant electrometer. In the first set of experiments, it was found that the maximum polarisation had occurred by the time the electrometer could be read, and the difference of potential was nearly equal to that obtained by joining the battery directly to the electrometer. Experiments with the open voltameter led to the conclusion that the difference of potentials between the plates remained nearly constant from the instant of making the current, but that the polarisation of the oxygen plate continuously *increased*, whilst that of the hydrogen plate *decreased*. In a voltameter free from air, the changes were similar, but in an opposite direction. The influence of a previous polarisation of the electrodes was examined, the battery being joined first in the same direction, and secondly in the reverse direction to that of the former current, and also the effect of polarisation of only one of the electrodes, this being effected by introducing temporarily a third electrode, and using it as an anode or cathode as required. By raising an electrode gradually out of the liquid, the effect of change of area was examined, and it was found that if either anode or cathode were raised so as to lessen its area of immersion, its polarisation was increased at the expense of the other.

Many other similar experiments were made, but without leading to any general conclusions, the author intending to extend the investigation, using gold and silver electrodes.

A. H. F.

Expansion of Mercury between 0° and −39°. By W. E. Ayrton and J. Perry (*Phil. Mag.*, **22**, 325—327).—By comparing the indications of a mercurial thermometer with those of a specially

constructed air thermometer (figured and described), the authors have found that the expansion of mercury from its freezing point to 0° C. is quite uniform; and that there is no critical point as in the case of water. Very great contraction, however, takes place when mercury passes from the liquid to the solid state. CH. B.

Heats of Formation of Potassium Alkyl Oxides. By DE FORCRAND (*Compt. rend.*, **104**, 68—71).—*Potassium propyl oxide*, C_3H_7OK, is obtained from normal propyl alcohol in the same way as the methoxide and ethoxide. Heat of solution at 12—15° = +14·92 cal.

C_3H_8O liq. + $\frac{1}{2}K_2O$ solid = C_3H_7OK solid + $\frac{1}{2}H_2O$ solid	develops	+ 22·55 cal.
C_3H_8O liq. + KHO solid = C_3H_7OK solid + H_2O solid	„	+ 2·06 „
C_3H_7OK solid + H_2O liq. = C_3H_8O liq. + KHO solid	„	− 0·63 „
C_3H_8O liq. + K solid = C_3H_7OK solid + H gas	„	+ 35·93 „
C_3H_7OK solid + nC_3H_8O liq. = C_3H_7OK diss. in nC_3H_8OH liq.	„	+ 11·75 „

Potassium isobutyl oxide, C_4H_9OK, is obtained from fermentation isobutyl alcohol in a similar manner, and alters very rapidly when exposed to air. Heat of solution +17·16 cal. The thermal disturbances resulting from the reactions corresponding with those given in the case of the preceding compound are +20·15 cal.; −0·34 cal.; +1·76 cal.; +33·53 cal.; and +8·89 cal. respectively.

Potassium amyl oxide, $C_5H_{11}OK$, forms white, silky crystals, which alter rapidly when exposed to air. It was prepared from fermentation amyl alcohol. Heat of solution +13·98 cal. The thermal disturbances corresponding with the five reactions given above are +23·27 cal.; +2·78 cal.; −1·35 cal.; +36·65 cal.; +8·59 cal.

The values obtained with these three compounds agree closely with those previously obtained with the methyl and ethyl derivatives. The differences are greatest in the case of the heats of solution of the solid compound in an excess of the corresponding alcohol, and these differences indicate a greater or less degree of dissociation of the poly-alcoholic alcoholates.

The following table shows the heats of formation of these compounds from their elements. The values agree closely except in the case of the last two compounds, which, however, are not derived from normal primary alcohols:—

K solid + H gas + O gas = HOK solid.	develops	+ 104·32 cal.
K solid + C (diamond) + H_3 gas + O gas = CH_3OK solid	„	+ 100·11 „
K solid + C_2 (diamond) + H_5 gas + O gas = C_2H_5OK solid	„	+ 106·18 „
K solid + C_3 (diamond) + H_7 gas + O gas = C_3H_7OK solid	„	+ 102·95 „

K solid + C_4 (diamond) + H_9 gas + O gas
= C_4H_9OK solid..... develops + 117·55 cal.
K solid + C_5 (diamond) + H_{11} gas + O gas
= $C_5H_{11}OK$ solid..... „ + 129·67 „

C. H. B.

Heat of Formation of Sodium Alkyl Oxides. By DE FORCRAND (*Compt. rend.*, **104**, 169—172).—*Sodium propyl oxide* is obtained in white, deliquescent crystals by dissolving sodium in propyl alcohol and heating the product at 200° in a current of dry hydrogen. Heat of solution +13·50 cal. A solution of the metal in excess of propyl alcohol, when allowed to evaporate in dry air, deposits crystals of the compound $PrONa + 2PrOH$, analogous to the compounds obtained under similar conditions with the methoxide and ethoxide.

Sodium isobutyl oxide is obtained in a similar manner in white, deliquescent crystals, which alter slightly in dry air. Heat of solution at +10° = 14·25 cal. If sodium is dissolved to saturation in isobutyl alcohol at 150° and the liquid allowed to cool, it deposits crystals of the trialcoholate, $C_4H_9ONa + 3C_4H_9OH$. The heat of solution of this compound is +17·31 cal., and hence

C_4H_9ONa solid + $3C_4H_9OH$ liq. = $C_4H_9ONa,3C_4H_9OH$ solid
develops + 5·56 cal.

Sodium amyl oxide, prepared in a similar manner, alters when exposed to dry air, although not to the same extent as the potassium compounds. Heat of solution = +14·21 cal. An alcoholate, $C_5H_{11}ONa + 2C_5H_{11}OH$, can be obtained in crystals.

The table contains the thermal disturbances corresponding with the following five reactions, and the last column gives the heats of formations of the solid compounds from the solid and gaseous elements. The corresponding values for the hydroxide, methoxide, and ethoxide are also given :—

(1.) ROH liq. + $\frac{1}{2}Na_2O$ solid = RONa solid + $\frac{1}{2}H_2O$ solid.
(2.) ROH liq. + NaHO solid = RONa solid + H_2O solid.
(3.) RONa solid + H_2O liq. = ROH liq. + NaHO solid.
(4.) ROH liq. + Na solid = RONa solid + H gas.
(5.) RONa solid + nROH liq. = RONa diss. in nROH liq.

	1.	2.	3.	4.	5.	
Hydroxide	+18·52	+1·43	+0·00	+33·30	+ 9·78	+102·30
Methoxide	+18·32	+1·32	+0·09	+33·19	+15·01	+ 95·22
Ethoxide	+17·35	+0·25	−1·19	+32·13	+12·40	+102·73
Propyl oxide....	+17·66	+0·65	+0·78	+32·52	+ 9·83	+ 99·56
Isobutyl oxide..	+16·76	−0·25	+1·68	+31·62	—	+115·66
Amyl oxide.....	+16·71	−0·30	+1·73	+31·57	—	+124·58

The variations in the values are similar to those previously observed in the case of the corresponding potassium compounds.

C. H. B.

Potassium Glyceroxide. By DE FORCRAND (*Compt. rend.*, **104**, 116—118).—92 parts of glycerol are added to a concentrated solution of 39·1 parts of potassium in absolute ethyl alcohol. Combination takes place rapidly, and the compound $C_3H_7KO_3$,EtOH separates in transparent lamellæ, which seem to belong to the orthorhombic or monoclinic system. A further quantity of the crystals can be obtained by concentrating the mother-liquor; they are rapidly decomposed by moist air.

The heat of solution of the compound in water is −0·06 cal. $C_3H_8O_3$ liq. + KOH solid + EtOH liq. = H_2O solid + $C_3H_7O_3K$,EtOH solid, develops +18·53 cal.

When heated at 120° in a current of dry hydrogen, the crystals lose alcohol and yield the glyceroxide $C_3H_7O_3K$. The heat of solution of this compound at +15° is +0·18 cal.

$C_3H_8O_3$ liq. + KHO solid = $C_3H_7O_3K$ solid + H_2O solid	develops	+ 15·84 cal.
$C_3H_7O_3K$ sol. + EtHO liq. = $C_3H_7O_3K$,EtOH solid	„	+ 2·69 „
$C_3H_8O_3$ liq. + $\frac{1}{2}K_2O$ solid = $C_3H_7O_3K$ solid + $\frac{1}{2}H_2O$ solid	„	+ 36·33 „
$C_3H_8O_3$ liq. + K solid = $C_3H_7O_3K$ solid + H gas	„	+ 49·71 „

The last value is higher than that obtained in the case of the sodium compound, and approaches the corresponding value for phenol.

$C_3H_8O_3$ liq. + EtOK diss. in *n*EtHO liq. = $C_3H_7O_3K$,EtOH diss. in *n*EtOH liq.	develops	+ 3·17 cal.

The direct formation of the simple glyceroxide would likewise be exothermic, but the development of heat (+0·46 cal.) would not be so great.

The values for potassium glyceroxide and its alcoholate are higher than those for the sodium compounds, except in the case of the heat developed by the union of the glyceroxide with the alcohol. This last result agrees with the fact that the alcoholate of potassium glyceroxide rapidly loses alcohol over sulphuric acid, whilst the sodium compound does not alter. The heats of formation of the two compounds from their elements are—

C_3 (diamond) + H_7 gas + O_3 gas + Na solid = $C_3H_7O_3Na$ solid	develops	+ 209·42 cal.
C_3 (diamond) + H_7 gas + O_3 gas + K solid = $C_3H_7O_3K$ solid	„	+ 215·23 „

C. H. B.

Thermal Properties of Ether. By W. RAMSAY and S. YOUNG (*Proc. Roy. Soc.*, **40**, 381—382).—In continuation of experiments on the physical constants of ethyl alcohol, the authors have made a similar study of ether, and numerical values have been obtained for the expansion of this liquid, the pressure of its vapour, and its compressibility in the gaseous and liquid states. From these results, the

densities of the saturated vapour and the heats of vaporisation have been deduced; the range of temperature of the observations is from −18° to 223°. The saturated vapour of ether, like that of alcohol, has an abnormal density, increasing with rise of temperature and corresponding rise of pressure. The critical temperature of ether seems to be 194°, the critical pressure 35·61 atmospheres; the volume occupied by 1 gram of the substance at 184° is 3·6 to 4 c.c. V. H. V.

Vapour-tension of Water from Salt Solutions. By W. W. J. Nicol (*Phil. Mag.*, **22**, 502—516). In 1835, Legrand (*Ann. Chim. Phys.*, **59**, 423) examined the effect of various salts in solution on the boiling point of water, and found that salts might be divided into those for which the quantity of salt necessary to produce a rise of one-half degree diminishes with the concentration (NaCl, KCl, &c.); those for which this quantity is fixed ($KClO_3$); those for which it increases with the concentration ($NaNO_3$, KNO_3, &c.); those for which it first diminishes, then is constant for a few degrees, and finally increases rapidly up to the point of saturation. The last was the most general case.

Legrand's results were incomplete and defective, in so far that the temperature was variable. Wüllner's experiments (*Ann. Phys. Chem.*, **110**, 564) have added little to the subject. In the author's experiments, the temperature was kept constant, and the tension of the vapour observed. Four salts, NaCl, KCl, $NaNO_3$, and KNO_3, which crystallise without water, were examined as follows: From 2 to 25 molecular proportions of the salt were dissolved in 100 molecular proportions of water, and the solution heated to boiling under diminished pressure in a flask provided with a condenser, and containing a large quantity of zinc to prevent superheating. The pressure was then allowed to rise slowly until the boiling point, measured by a thermometer with its bulb completely immersed in the liquid, rose to 70°. At intervals of 5° from 70° to 95°, the pressure was observed, and the difference between this pressure, p', and the vapour-tension of pure water, p, at the same temperature, also measured by a submerged thermometer, showed the "restraining effect" of n molecules of the salt. The quantity $\frac{p-p'}{n}$ was the restraining effect for each molecule at the particular temperature. Tables of these values for the various temperatures are given, and from these the following conclusions may be drawn.

The restraining effect of each salt molecule increases with the concentration in the case of sodium chloride, and less markedly so in the case of potassium chloride. For sodium nitrate, it diminishes as concentration increases, and still more so for potassium nitrate.

Rise of temperature diminishes the restraining effect of sodium chloride, leaves that of potassium chloride unaffected, increases that of sodium nitrate, and still more increases that of potassium nitrate.

When both temperature and concentration increase, the salts form the same series; that is, there is diminution of the restraining effect of sodium chloride, less of that of potassium chloride, little or none of that of sodium nitrate, but marked increase of that of potassium nitrate.

When the solubility as a function of the temperature is considered, the same order is preserved. That of sodium chloride increases slightly with the temperature; that of potassium chloride rather more; that of sodium nitrate to a still greater extent; whilst that of potassium nitrate increases enormously.

There is clearly a connection between increase of solubility and restraining effect.

Some of these results are directly opposed to those obtained by Wüllner, who found that the total effect was in all cases in direct proportion to the amount of salt dissolved; but they agree satisfactorily with those of Tammann (Abstr., 1885, 862), with which the author compares them.

The author points out that these results are in accordance with his theory of solution (Abstr., 1884, 253). According to this, solution results from the tendency towards equilibrium of three forces, attraction of water for water, and of salt for salt (cohesions), and attraction of salt for water (adhesion). These three forces may be unequally affected by rise of temperature; and accordingly as difference between adhesion and the sum of cohesions at any temperature is $> = <$ the same difference at a lower temperature, so is solubility $> = <$ solubility at a lower temperature. Now the restraining effect per molecule is seen from the tables to be nearly the same for the four salts in *dilute* solution; or, for $n = 2$, $\frac{p - p'}{n}$ for NaCl = 4·25, for KCl = 3·8, for $NaNO_3$ = 4·25, for KNO_3 = 3·75. In *strong* solutions it is very different. Now the heat of solution is as follows:—NaCl = −1180, KCl = −4400, $NaNO_3$ = −5200, KNO_3 = −8500; regarding this as a measure of the work done in effecting a change of state, it is evident that the cohesion of the salts increases from sodium chloride to potassium nitrate. It may reasonably be supposed that concentration has but little effect on the attraction for water of a salt having small cohesion; but that it slowly diminishes this attraction when the cohesion is large, until saturation is reached. The influence of concentration is thus accounted for.

With regard to the effect of rise of temperature, it is evident that all three forces will be thereby diminished. If the cohesions be diminished a little more than the adhesion, the salt will be more soluble, and its restraining effect diminished at the higher temperature. But if the cohesions be large, and largely diminished by rise of temperature, the *comparative* value of the adhesion will be increased, and increase of restraining effect will result. Ch. B.

Vapour-tension of Sodium Acetate. By H. Lescœur (*Compt. rend.*, **104**, 60—63).—Sodium acetate and water will furnish three distinct systems, the first of which is prepared at the ordinary temperature with the crystallised salt $NaC_2H_3O_2 + 3H_2O$; the second with the fused and dehydrated salt; and the third by heating the two first systems to complete solution, and then cooling the liquids. Determinations of the maximum vapour-tensions of the three systems at 20° indicate the existence of at least three isomeric systems, but as soon as the quantity of water present becomes sufficient for complete

solution, the three systems merge into one. It follows, therefore, that the differentiation takes place only at the moment of a change in the physical conditions of the systems.

The vapour-tension of a solution of sodium acetate diminishes regularly in proportion to the amount of anhydrous sodium acetate dissolved, and since, according to Wüllner, the diminution in the maximum vapour-tension is proportional to the weight of the compound actually existing in the system, it follows that the solution of sodium acetate contains the anhydrous salt almost exclusively.

The second system, which corresponds with the saturation of the solution, has a constant maximum vapour-tension of 12·4 mm., but when the composition of the system approaches that of the hydrate, $NaC_2H_3O_2 + 3H_2O$, the tension drops suddenly to 4·4 mm., and retains this value until dehydration is complete.

The maximum vapour-tension of the hydrated salt, $NaC_2H_3O_2 + 3H_2O$, increases with the temperature up to 58°, at which point the salt melts. The water is given off as a whole, and no intermediate hydrates are formed. The tension of dissociation of the hydrate is lower, and the maximum vapour-tension of its saturated solution is higher than the average tension of the aqueous vapour in the atmosphere, hence the hydrate is neither efflorescent nor deliquescent. As the vapour-tension of the saturated solution of anhydrous sodium acetate is lower than the average tension of atmospheric aqueous vapour, anhydrous sodium acetate is deliquescent.

These results explain Reischauer's observations concerning the hydration of sodium acetate (*Ann. Chim. Pharm.*, **95**, 116).

C. H. B.

Relation between the Theories of Capillarity and of Evaporation. By J. Stefan (*Ann. Phys. Chem.* [2], **29**, 655—665). —Laplace has based his theory of capillarity on the assumption that there is a force of attraction between the particles of a liquid which decreases very rapidly with the distance, becoming insensible at a certain small distance known as the radius of molecular attraction. From this it follows that the molecular forces acting on a particle are in equilibrium so long as the distance of the particle from the liquid surface exceeds the above, but that if it is less, they have a resultant inwards, and consequently an expenditure of work is required to transfer liquid from the interior to the surface. Adopting Clausius' theory of evaporation, and assuming that the particles of a liquid do not differ from those of its vapour, it is shown that in the case of a plane surface the work done in moving a particle from the interior to the surface, is equal to that required to transfer it from the surface into the vapour above it. This work is equivalent to the heat required for the process. If the density of the liquid were uniform up to the boundary between it and its vapour, the equation $p_2 - p_1 = \rho A$ would give the relation between p_2, the pressure in the interior, p_1 the pressure at the surface, ρ the density, and A the mechanical equivalent of the latent heat of evaporation of the liquid, a relation which in the case of ether gives for p_2, 2574 atmospheres! Assuming that the density is a linear function of the pressure, a similar though

somewhat smaller result is obtained, as well as a value of $p_2 = 2728$ atmospheres for carbon bisulphide. It is important, however, to mark that the above results are based on the assumption that no work is expended on the molecule itself in transferring it from the liquid to the vapour.

The author also explains on this theory the fact, first noticed by Sir W. Thomson, that the pressure of saturated vapour is less in the presence of a concave liquid surface, and greater in the presence of a convex, that when the surface is plane. A. H. F.

Coefficients of Affinity of Bases. By W. Ostwald (*J. pr. Chem.* [2], **35**, 112—121).—In this paper, the author determines the coefficients of affinity of various bases by means of the rate of hydrolysis of ethyl acetate, and compares the results with those obtained from the corresponding coefficients of electrical conductivity. The following results were obtained:—

	Dynamical.	Electrical.
Potash	161·0	161·0
Soda	162·0	149·0
Lithia	165·0	142·0
Thallium hydroxide	158·0	156·0
Ammonia	3·0	4·8
Methylamine	19·0	20·2
Ethylamine	19·0	20·5
Propylamine	18·6	18·4
Isobutylamine	14·4	15·2
Amylamine	18·5	18·6
Allylamine	4·0	6·9
Dimethylamine	22·0	23·5
Diethylamine	26·0	28·3
Trimethylamine	7·3	9·7
Triethylamine	22·0	20·2
Piperidine	27·0	27·0
Tetraethylammonium hydroxide	131·0	128·0

The discrepancies in the case of the feeble bases, ammonia and allylamine, are probably due to the difficulty of obtaining the coefficient of initial change by interpolation. H. K. T.

Influence of Heat on the Decomposition of Oxalic Acid by Ferric Chloride. By G. Lemoine (*Bull. Soc. Chim.*, **46**, 289—294).—The author formerly investigated (Abstr., 1884, 381) the influence of sunlight on the progress of the reaction $Fe_2Cl_6 + H_2C_2O_4 = 2FeCl_2 + 2HCl + 2CO_2$. He now describes the action of heat on the same reaction. The aqueous solutions used contained 63 grams of crystallised oxalic acid and 162·5 grams ferric chloride respectively per litre. When equal volumes of these were solutions heated together in the dark, scarcely any action took place until the temperature reached 50°, the action then increased rapidly as the temperature was increased. At 100°, the evolution of gas

was at first rapid, gradually decreasing in the same ratio as the oxalic acid remaining undecomposed in the mixture decreased. Dilution with water very much increased the evolution of gas. The author considers this to be due to the action of the water in decomposing the ferric chloride, and thus assisting the formation of ferric oxalate, which is then further decomposed. Dilution with normal solutions of ferric chloride, ferrous chloride, or hydrochloric acid had scarcely any influence on the rate of reaction, the additional water in these cases not acting as if in the free state. Dilution with normal oxalic acid greatly increased the rate of reaction until enough oxalic acid had been added to form an acid ferric oxalate (the colour changing to green), but further addition of oxalic acid gradually diminished the rate of reaction. The author has not succeeded in isolating the acid oxalate which appears to be formed.

The influence of heat on this reaction seems, therefore, to be similar to that of light. L. T. T.

Theory of Fractional Precipitation. By J. J. Hood (*Phil. Mag.* [5], **21**, 119—127). When the separation of the rarer closely allied earths is effected either by decomposition of the nitrates by heat, or by precipitation of highly dilute solutions by ammonia, the relative amount of each salt decomposed depends on its "basic power," or coefficient of resistance to decomposition; a quantity which may or may not vary with the temperature, and with the nature of the precipitant. In any separation, it is of importance to determine the conditions for the greatest difference of basic powers. In practice, the basic power, E, might be determined by measuring the intensity of the action when the same amount of precipitant is added to solutions each containing a definite mass of some sulphate (Ni, Co, Mn); or, by the action of the precipitant on a solution containing one or more of these sulphates, the relative values of E might be arrived at. In these cases, E might be regarded as a measure of the attraction of a particular base for a particular acid.

In the following theoretical investigation, no account is taken of secondary or inverse actions. Let the masses of two salts in solution be A and B, and let E and E′ be the respective basic powers. Assuming that the rate of precipitation is proportional to the products of the active materials in solution, let x of A and y of B be precipitated at time t, and let p and q be quantities of precipitant consumed in each case. Then

$$\frac{dx}{dt}=\frac{1}{\mathrm{E}}(\mathrm{A}-x)(\mathrm{C}-p-q) \text{ and } \frac{dy}{dt}=\frac{1}{\mathrm{E}'}(\mathrm{B}-y)(\mathrm{C}-p-q),$$

from which

$$\left(1-\frac{x}{\mathrm{A}}\right)^{\mathrm{E}}=\left(1-\frac{y}{\mathrm{B}}\right)^{\mathrm{E}'} \text{ or } \frac{\mathrm{E}}{\mathrm{E}'}=\frac{\log\left(1-\frac{y}{\mathrm{B}}\right)}{\log\left(1-\frac{x}{\mathrm{A}}\right)}.$$

Thus the ratio $\frac{\mathrm{E}}{\mathrm{E}'}$ should be calculable from a single experiment,

and should be independent of the time taken by the precipitate to form, and of the mode of addition of the precipitant. It can also be shown that the ratio of the less to the more basic material in the precipitate increases, the smaller the fraction precipitated; and if the ratio of the salts in solution be V, the maximum value of the preceding ratio will be $\frac{E}{VE'}$ for an infinitesimal precipitate. If $E = E'$, no separation is possible; the experiments of Marignac (Abstr., 1884, 813) are not therefore decisive as regards the homogeneous character of the commoner elements.

Taking some observations by Mills and Bicket (Abstr., 1882, 689) on the precipitability of manganese and nickel sulphates by dilute sodium carbonate, the author finds the value of $\frac{E}{E'} = 2{\cdot}97$; that is, the former resists the decomposing action of sodium carbonate with a force 2·97 times greater than does the latter. Similarly for nickel and cobalt sulphates, precipitated by dilute aqueous soda (Mills and Smith, Abstr., 1879, 877) $\frac{E}{E'} = 0{\cdot}97$. The separation of these two metals by fractional precipitation in this way would therefore be extremely tedious.

The author shows, however, that basic power is not related to atomic weight, as might be suspected. Debus (*Annalen*, **85**, **86**, and **87**) found that if a solution containing baryta and lime in the ratio α is precipitated by carbonic anhydride, the ratio of the oxides in the precipitate is given by the equation $\alpha = K\beta$. For a *small* precipitate $K = \frac{E}{E'}$ approximately.

Ch. B.

Halogen Carriers. By L. Meyer (*J. pr. Chem.* [2], **34**, 502—504).—The author does not agree with Wildgerodt that the property of transferring halogens is a function of the atomic weights of the elements, provided they form the necessary combinations (compare this vol., p. 130). Thus antimony acts in this way, bismuth does not. The author maintains his view that a combination first takes place between the haloid compound and the substance acted on, that a combination then takes place between the halogen of the double compound and the hydrogen of the same, their places being taken by the free halogen. He quotes several reactions in support of his view.

H. K. T.

Halogen Carriers. By C. Willgerodt (*J. pr. Chem.* [2], **34**, 547—550).—A reply to L. Meyer (preceding Abstract). The author points out the difference in the methods employed by himself and those used by Meyer and his pupils.

G. H. M.

Indium and Gallium as Halogen Carriers. By C. Willgerodt (*J. pr. Chem.* [2] **35**, 142—144).—The author continues his researches on halogen carriers. With metallic indium in benzene, scarcely any chlorination took place until the indium had been converted into the chloride by the small quantity of hydrogen chloride formed. The

chlorination then proceeded rapidly. The product consisted almost entirely of paradichlorobenzene. With gallium, the chlorination commenced at once; mono- and di-chlorobenzene and a small quantity of benzene hexachloride were produced. The author regards these experiments as giving further evidence of his law that the halogen carrying power of an element is a function of its atomic weight provided it form the necessary combination. H. K. T.

Expansion produced by Amalgamation. By W. E. Ayrton and J. Perry (*Phil. Mag.*, **22**, 327).—A brass bar, one foot long and three-quarters of an inch thick, rapidly became curved when it was amalgamated along one edge, this edge becoming convex; and on hammering the bar to straighten it the curvature increased. Very great force must be produced by amalgamation.

The authors think that the mercury amalgam used in polishing Japanese "Magic Mirrors" may assist in making the thin portions more convex than the thicker. Ch. B.

Inorganic Chemistry.

Oxy-acids of Iodine. By C. W. Blomstrand (*J. pr. Chem.* [2], **34**, 433—462).—A review of the evidence pointing to the pentavalent nature of iodine in periodic acid.

Production of Ozone. By J. J. Thomson and R. Threlfall (*Proc. Roy. Soc.*, **40**, 340—342).—Experiments were made with a view of ascertaining whether ozone is produced in an electric field, just not strong enough to permit of the passage of the spark through oxygen gas. The gas, before passing into the ozonising apparatus, was carefully dried and purified, and the issuing gas tested with paper soaked with a most sensitive solution of potassium iodide and starch, as also by the solution itself. Practically no ozone was produced.

It is further shown that no ozone is produced when a spark is passed through oxygen dried with the utmost care. V. H. V.

Action of Sulphur on Ammonia and Metallic Bases in Presence of Water. By J. B. Senderens (*Compt. rend.*, **104**, 58—60).—Contrary to Brunner's statement, an aqueous solution of ammonia of ordinary concentration acts gradually on sulphur at the ordinary temperature, with formation of a dark red liquid which contains a polysulphide and a thiosulphate. If this solution is exposed to the air, it deposits sulphur. The same products are formed according to Fluckiger, when sulphur is heated at 100° with ammonia in sealed tubes for several days.

Barium and calcium oxides likewise act on sulphur in the cold in

presence of water, forming a solution containing a polysulphide and a thiosulphate. When silver oxide or lead monoxide is heated with sulphur and water in a sealed tube at 100°, a sulphide and a sulphate are formed in accordance with the equation $4MO + S_4 = 3MS + MSO_4$. Both lead and silver oxides are slightly soluble in water, but similar reactions are obtained with triplumbic tetroxide, mercuric oxide, and cupric oxide. The formation of the sulphides under these conditions corresponds with a considerable development of heat. This is not, however, the only determining cause of the reaction, since ferric oxide is only very slightly affected by sulphur, and zinc oxide is not affected at all. The heats of formation of these oxides are, however, much higher than the heats of formation of the oxides of mercury, copper, &c., and it would seem therefore as if the decomposition of metallic oxides by sulphur in presence of water were partly conditioned by the absolute value of the heat of formation of the oxide. C. H. B.

Combination of Sulphuric Anhydride with Phosphoric and Iodic Anhydrides. By R. Weber (*Ber.*, **20**, 86—88).—When a mixture of pure sulphuric anhydride with phosphoric anhydride is heated in a right-angled tube at 100° for a short time, combination ensues, and, after decanting the fluid portion into the empty limb, and cooling, thin, transparent scales of a compound, $P_2O_5 + 3SO_3$, are obtained (this vol., p. 212); these can be freed from excess of sulphuric anhydride by carefully heating them at 30° and allowing them to drain. The compound readily decomposes when heated above 30°; the residue, however, still retains some sulphuric anhydride at higher temperatures.

Sulphuric anhydride and iodic anhydride combine under similar conditions to form a compound, $I_2O_5 + 3SO_3$, sparingly soluble in sulphuric anhydride, and crystallising in lustrous, yellow scales. It is more stable than the phosphorus compound, and can be heated to 60° without decomposition; at higher temperatures, sulphuric anhydride distils off although the residue still retains a certain proportion at 100°. W. P. W.

Passage of Electric Discharge through Pure Nitrogen. By J. J. Thomson and R. Threlfall (*Proc. Roy. Soc.*, **40**, 329—340).—It is observed that when a succession of electric sparks is sent through a sealed discharge tube containing nitrogen at a pressure less than 20 mm. of mercury, a permanent diminution of the nitrogen takes place, which ultimately reaches a maximum of 8 to 12 per cent. of the original volume if the pressure be 8 mm., but only 2 to 3 per cent. with a pressure of 16 mm. A considerable time is required before this maximum value is attained, and the ratio of this diminution to the original volume is independent of the volume of the discharge tube, the extent of its surface, and the substance of the electrode, whether platinum or aluminium. If the tube is maintained at a temperature of over 100° for several hours, the gas regains its original volume.

The apparatus is described in full, as also the method used for the preparation of the nitrogen, the determination of the quantity of

oxygen contained in the gas and the elimination of hydrogen from the electrodes as evidenced by spectroscopic examination. It was proved that the gas used contained less than 1 part in 800 of oxygen, whilst the contraction observed would require the presence of 15 per cent. of hydrogen if this gas combined with the nitrogen to form ammonia, whereas only the minutest traces of hydrogen could be detected by means of the spectroscope. The authors incline to the hypothesis that an allotropic modification of nitrogen is produced by the sparking, and the phenomena of the contraction of volume and expansion on heating are analogous to those observed in the case of ozone. It is further noticed that when the discharge passes through nitrogen, whose pressure has been diminished by sparking, it shows a greater tendency to produce a beautiful golden colour than when it passes through a tube recently filled. No attempts have thus far been made to ascertain the chemical properties of this modified gas.

V. H. V.

Note.—G. S. Johnson, in a pamphlet entitled "Elementary Nitrogen," has described the production of an allotropic modification of this gas under conditions somewhat similar to those mentioned above.—V. H. V.

Hydrated Silicon Phosphate. By P. Hautefeuille and J. Margottet (*Compt. rend.*, **104**, 56—57).—If a concentrated solution of phosphoric acid containing about one quarter of the quantity of silica required to saturate it, is heated at 125° for 7 or 8 days, it deposits concretions which gradually increase in size. They are separated from the mother-liquor by pouring the hot liquid on to a previously heated porous plate, and are dried by exposure to dry air for about a week. The spherical globules thus obtained have the composition $SiO_2,P_2O_5,4H_2O$. When suspended in sulphuric acid, they act strongly on polarised light, showing black crosses with the arms in the principal planes of the Nicols. Under the microscope, the concretions are seen to be formed of concentric cones of prismatic crystals with their principal axes radiating from the centre. The silicon phosphate decomposes rapidly in moist air, and dissolves completely in water at 0°, but is decomposed by water at the ordinary temperature, with separation of gelatinous silica. C. H. B.

Action of Carbon Tetrachloride on Metallic Oxides. By E. Demarçay (*Compt. rend.*, **104**, 111—113).—Niobic anhydride is slowly attacked by vapour of carbon tetrachloride at 220°, but very rapidly at 440°, the products being niobic chloride, carbonic chloride, and carbonic anhydride. Titanic oxide is also very readily attacked at 440°, and in fact titanium tetrachloride can readily be prepared by the action of carbon tetrachloride vapour on fragments of rutile heated to dull redness in a somewhat long, hard glass tube. When titanic oxide and carbon tetrachloride are heated together in sealed tubes, it is found that the reaction really occurs in three phases, which are severally represented by the equations $TiO_2 + CCl_4 = TiOCl_2 + COCl_2$; $TiOCl_2 + COCl_2 = TiCl_4 + CO_2$; $TiOCl_2 + CCl_4 = TiCl_4 + COCl_2$. Titanium oxychloride is a yellow crystalline solid.

In addition to carbonic anhydride and carbonyl chloride, which are formed with all the oxides, some carbon hexachloride and free chlorine are amongst the products of this reaction.

Chromic, aluminium, and tantalic oxides are readily attacked under similar conditions. Zirconia is only slowly attacked at 440°, but rapidly at dull redness. Silica is scarcely affected even at the higher temperature.

Zircons are not attacked by carbon tetrachloride. Certain opaque Swedish specimens became transparent after heating in the vapour, most probably in consequence of the removal of small quantities of titanium, niobium, &c. C. H. B.

Action of Carbon Tetrachloride on Chromyl Dichloride and Ferric Phosphate. By H. Quantin (*Compt. rend.*, **104**, 223—224).—Nickel and cobalt oxides, and tungstic and molybdic anhydrides are readily converted into chlorides when heated in the vapour of carbon tetrachloride. At the same time, this process has no advantages over the method of preparing anhydrous chlorides by the action of a mixture of chlorine and carbonic oxide on the respective oxides. Silicon dioxide and boron trioxide are not affected in either case.

The author has previously found that carbonic oxide decomposes chromyl dichloride into chromic oxide and chromic chloride. A similar reaction takes place between chromyl dichloride and carbon tetrachloride, as expressed by the equation $2CrO_2Cl_2 + 4CCl_4 = Cr_2Cl_6 + 4COCl_2 + 3Cl_2$. Some carbonic anhydride is also formed.

When carbon tetrachloride vapour is passed over heated ferric phosphate, violet vapours are produced, and if these are passed over a column of granular potassium chloride heated at 200°, the ferric chloride is absorbed, and yellow crystals are deposited on the cold part of the tube; these crystals are very hygroscopic, and have an irritating odour; their aqueous solution deposits carbon tetrachloride and contains hydrochloric acid and phosphoric acid. Analysis shows that the crystals are phosphorus pentachloride. With more basic phosphates the reaction is similar, but it seems to be different with the phosphate $3P_2O_5,2Fe_2O_3$.

When a boat or dish is used, a somewhat large excess of carbon tetrachloride is required for complete decomposition. It is therefore better to mix the ferric phosphate with carbon from sugar and place the mixture in a layer in front of a layer of potassium chloride.

C. H. B.

Sodium Carbonate. By W. Smith and W. B. Hart (*J. Soc. Chem. Ind.*, **5**, 643—644).—The authors have investigated an alleged reaction, on which is based a recently patented process for manufacturing sodium carbonate directly from sodium sulphate, and draw the following conclusions from the results of their researches:—(1.) No action takes place at a dull red heat when carbonic oxide comes in contact with sodium sulphate in a glass tube, even in presence of moisture. (2.) At a bright red heat, in presence of moisture, sodium sulphite and sulphide are produced. (3.) At a bright red heat, moreover, the silica of the glass reacts with the sulphite and sulphide, especially in presence of moisture, yielding silicate, sulphurous

anhydride, and hydrogen sulphide. (4.) From the fact that no sulphurous anhydride could be detected but only hydrogen sulphide, it is inferred that reduction by carbonic oxide tends, under the circumstances named, to convert the sulphate directly to sulphide. (5.) The proportion of this reduction is very small, even at a bright red heat. (6.) No carbonate was formed under any of the conditions mentioned. (7.) In absence of moisture and with carbonic anhydride in slight excess over that necessary to form a volume equal to that of the carbonic oxide in the gas mixture, a bright red heat being employed, no reduction of sulphate took place. (8.) Carbonic oxide at a bright red heat and in presence of moisture, reduces sulphurous anhydride to sulphur. If moisture is excluded this reduction does not proceed quite so easily. D. B.

Occasional Products in the Soda Manufacture. By C. Rammelsberg (*J. pr. Chem.* [2], **35**, 97—111).—The following compounds were obtained from the hearth of a Leblanc soda-ash furnace.

Aluminium calcium silicate combined with calcium sulphide, $2CaS,6Ca_3SiO_5,Al_2SiO_5$, yellow or green, transparent, prismatic crystals; $a:c = 1:0{\cdot}58318$. Calcium silicate, $CaSiO_3,Ca_2SiO_4 + H_2O$, small, hard, white, pointed prisms. White octahedral crystals, which in a few days fell to powder, and consisted of calcium hydroxide mixed with carbonate.

In an iron clearing-vat, crystals were found having the composition, $Na_2CO_3,CaCO_3 + 5H_2O$, and identical with gay-lussite. H. K. T.

Influence of Heat on the Combination of Water of Crystallisation with Sodium Monosulphide. By C. Göttig (*J. pr. Chem.*, [2], **35**, 89—91).—The author has previously shown that when hydrated sodium sulphide separates from alcoholic soda treated with hydrogen sulphide, products with varying percentages of water of crystallisation are obtained. Experiments described in the present paper confirm this, and show that the percentage of water of crystallisation depends not only on the strength of the alcohol, but also on the temperature at which the sulphide is prepared. At temperatures between 17° and 22°, a hydrate containing 6 mols. H_2O was formed; at 41° to 45°, a hydrate containing $5\frac{1}{2}$ mols. H_2O. N. H. M.

Silver Ammonio-nitrate. By H. N. Draper (*Pharm. J. Trans.*, [3], **17**, 487—488).—The precipitate first formed when ammonia is added to a solution of silver nitrate, is silver oxide, which is soluble in ammonium nitrate. Therefore only a small proportion of the silver is at any time precipitated, and if any free nitric acid is present, ammonia fails to produce any precipitate. A further addition of ammonia results, as is well known, in the formation of silver ammonio-nitrate. D. A. L.

Action of Non-metals on Solutions of Silver and Cupric Nitrates. By J. B. Senderens (*Compt. rend.*, **104**, 175—177).—Powdered selenium acts more readily than sulphur on boiling aqueous solutions of silver nitrate, reduction being almost complete,

even when the solution is somewhat concentrated. The reaction takes place in accordance with the equation $4AgNO_3 + 3Se + 2H_2O = 2Ag_2Se + SeO_2 + 4HNO_3$. If the substances are heated together in sealed tubes, the action is almost complete, but a certain quantity of silver selenite is formed, and dissolves in the hot liquid, but separates in white needles on cooling.

The action of powdered tellurium at 100° is similar to that of selenium but somewhat less rapid. In sealed tubes, however, the precipitation of the silver by tellurium is always complete, and if the tellurium is in excess, the nitric acid which is formed is decomposed with production of nitrogen peroxide even in dilute solutions.

Silver nitrate in solution is completely, although slowly, reduced by selenium and tellurium at the ordinary temperature. Cupric nitrate is not affected under the same conditions, but is partially reduced by tellurium on heating.

The reduction of silver nitrate by arsenic yields arsenious and not arsenic acid, and takes place in accordance with the equation $3AgNO_3 + As + 3H_2O = Ag_3 + H_3AsO_3 + 3HNO_3$. The precipitate is free from arsenic.

The action of amorphous phosphorus on solutions of silver and copper nitrates respectively is represented by the equations $5AgNO_3 + P + 4H_2O = 5Ag + H_3PO_4 + 5HNO_3$, and $5Cu(NO_3)_2 + P_6 + 8H_2O = Cu_5P_4 + 2H_3PO_4 + 10HNO_3$. A solution of copper nitrate yields the compound Cu_5As_2 when treated with arsenic. Solid iodine acts on silver nitrate solution in the dark in accordance with the equation $5AgNO_3 + I_6 + 3H_2O = 5AgI + HIO_3 + 5HNO_3$, and the action of bromine is represented by the equation $AgNO_3 + Br_2 + H_2O = AgBr + HBrO + HNO_3$, as previously stated by J. Spiller and Schönbein. C. H. B.

Reaction between Barium Carbonate and Sodium Sulphate under the Influence of Pressure. By W. Spring (*Bull. Soc. Chim.*, **46**, 299—302).—The author has already shown (*Bull. Soc. Chim.*, **44**, 166) that when an intimate mixture of sodium carbonate and barium sulphate is subjected to intense pressure, a considerable amount of double decomposition occurs. He has now studied the reverse action. When finely powdered dry sodium sulphate and barium carbonate are intimately mixed in molecular proportions and the mixture subjected to pressure, a considerable quantity of barium sulphate is produced. If the mixture is shaken for some time in a dry flask, about 50 per cent. of the barium carbonate is found to have become converted into sulphate. If the mixture is subjected to a single pressure of several thousand atmospheres, the percentage of barium sulphate is increased to about 60 per cent. Subjected to thrice repeated pressure—the compressed mass being re-powdered before each renewed pressure—the percentage of barium sulphate is increased to about 70 per cent., and after six similar renewals of pressure to about 73 per cent. If the mixture under ordinary atmospheric pressure is allowed to remain untouched, no further increase of barium sulphate takes place, but if the mixture is maintained under pressure the formation of barium sulphate increases until a limit of about 80·5 per cent. is reached.

When fragments of the compressed cylinders were heated at 160° for some hours and then again analysed, the percentage of barium sulphate was found to have been very much diminished. The author intends further to investigate this influence of heat; and also the double decomposition of mixtures of dry substances under ordinary pressures. He finds that when dry copper sulphide is shaken with dry silver nitrate, double decomposition takes place. L. T. T.

Calcium Silicostannate. By L. Bourgeois (*Compt. rend.*, **104**, 231—233).—Three parts of silica and four parts of stannic oxide are heated with an excess of calcium chloride to bright redness for about eight hours, and the cooled mass extracted with water. If the time of fusion has been short, the residue is a mixture of tridymite and cassiterite, but if the reaction has proceeded further the residue consists of calcium silicostannate, whilst if the heating has been too far prolonged, the products are calcium bisilicate and calcium stannate.

Calcium silicostannate, CaO,SiO_2,SnO_2, analogous to sphene, is obtained as a brilliant white powder consisting of monoclinic prisms somewhat less birefractive than those of sphene; sp. gr. 4·34. They are not attacked by acids, potassium hydrogen sulphate, or solutions of alkalis, and are less fusible than sphene.

A mixture of silica, stannic oxide, and titanic oxide, with calcium chloride, yields similar crystals, which contain all three of the dioxides. Crystals of cassiterite form on the upper part of the crucible, and if the action is prolonged icositetrahedrons of the composition $3CaO,Al_2O_3,3SiO_2$ are formed by the action of the fused mixture on the crucible. C. H. B.

Solubility of Gypsum in Solutions of Ammonium Salts. By S. Cohn (*J. pr. Chem.* [2], **35**, 43—56).—Droeze has already shown (this Journal, 1877, ii, 112) that the solubility of gypsum in solutions of salts decreases with the concentration of the salt solution, except in the case of ammonium nitrate solution, when the solubility first increases and then decreases. The author has determined the solubility of gypsum in solutions of different ammonium salts of varying strength. The results of several experiments point to the following conclusions:—1. The irregularity observed by Droeze in the case of ammonium nitrate exists also in the case of the chloride, but not in the case of the sulphate; this difference is possibly due to a chemical reaction taking place with the gypsum. 2. Ammonium sulphate increases the solubility of gypsum, probably forming readily soluble double salts. 3. Ammonium chloride, nitrate, and acetate, increase the solubility of gypsum by double decomposition, readily soluble calcium salts being formed. 4. The decomposition of the gypsum by the ammonium salts increases with decreasing concentration. 5. Gypsum dissolves most readily in ammonium acetate, then in nitrate, chloride, and sulphate. 6. This order holds good for the readiness with which gypsum is decomposed by the salts.

The methods employed in preparing the solutions and determining the amount of gypsum are described. N. H. M.

Crystallography of Cadmium Borotungstate. By G. Linck (*Zeit. Kryst. Min.*, **12**, 442—446). — Two kinds of crystals are obtained from the concentrated solution of cadmium borotungstate, which, according to Klein (Abstr., 1881, 1168), has the composition $9WO_3B_2O_3,2CdO + 18H_2O$. The crystals which separate out first are of a bright yellow colour and tabular in form (Analysis I); whilst the others are of a yellowish-brown colour, and have a pyramidal form (Analysis II). Analysis gave the following results:—

	H_2O at 100°.	H_2O at red heat.	CdO.	WO_3.	B_2O_3.	Total.
I.	8·18	4·18	9·33	76·27	2·04	100·00
II.	8·03	3·80	9·52	76·51	2·14	100·00

Neither of the salts analysed correspond with Klein's formula, in that they contain much less water of crystallisation and more chemically combined water.

The yellow crystals belong to the monosymmetric system; the axial ratio being $a : b : c = 1·3321 : 1 : 1·1383$; $\beta = 57° 47'$. The forms observed were 0P, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, $\breve{P}\infty$, $\breve{P}\infty$, $6\breve{P}\infty$.

The brown crystals belong to the asymmetric system; $a : b : c = 0·6261 : 1 : 0·4398$. $\alpha = 114° 56'$; $\beta = 92° 47'$, $\gamma = 94° 57'$. The following planes were observed:—0P, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $\infty'\breve{P}\frac{5}{4}$, $\infty P'$, P, $\frac{1}{2}\frac{9}{0}P'$. B. H. B.

Higher Oxides of Copper. By T. B. Osborne (*Amer. J. Sci.* [3], **32**, 333—342).—The various coloured hydrated oxides of copper obtained by treating cupric hydroxide with hydrogen peroxide, are all mixtures in varying proportions of the brown dioxide, CuO_2,H_2O, with cupric hydroxide. The author has also experimented on the so-called sesquioxide, obtained by the action of alkaline solutions of hypochlorites on copper compounds, but has not obtained any conclusive results. A. J. G.

New Elements in Gadolinite and Samarskite. By W. Crookes (*Proc. Roy. Soc.*, **40**, 502—509). — An account of the differentiation in the absorption and the phosphorescent spectra obtained by the process of systematic fractionation of the earths present in gadolinite and samarskite. By the evidence of absorption spectra, Welsbach has concluded that didymium is separable into two elements, designated præsodymium and neodymium, which give green and rose-red salts respectively. The method adopted by the author does not lead to the same conclusion, although it is suggested that didymium can be resolved in more than one direction according to the method adopted. Evidence has, however, been afforded of a blue line, λ451·5, characteristic of the element named dysprosium by Boisbaudran, as also of absorption-bands λ475 and λ443, which can be obtained separate from λ451·5, and thus belong to some element.

By systematic fractionation, and examination of the various portions by the phosphorescent spectrum method, it is shown that the spectrum bands hitherto considered to belong to yttria vary in intensity among themselves, as also that the element called Yα or gadolinium,

by Marignac, is probably composed of at least four simpler substances. The spectrum of this $Y\alpha$ is that of yttria with the chief characteristic, namely, the citron band, left out, and with the double green band of samaria added to it. A provisional list is given of eleven elements, inclusive of ytterbium and gadolinium, with the mean wave-lengths of their dominant band.

Attention is also drawn to the delicacy of the phosphorescent spectrum method as applicable to substances which have been approximately separated but not yet completely isolated by chemical processes. In accuracy, it is unsurpassed by spectrum analysis; in economy, it possesses the advantage that the specimen examined is not destroyed, whilst continued experience confirms its trustworthiness.

V. H. V.

Note.—For a further account of the experiments described above and the theoretical conclusion drawn therefrom, compare the address of the author to the Chemical Section of the British Association, Report, 1886.—V. H. V.

Chemistry of Manganese and of Fluorine. By O. T. Christensen (*J. pr. Chem.* [2], **35**, 57—82; comp. Abstr., 1886, 854). —When chlorine is passed into absolute ether containing pure manganese peroxide in suspension and cooled by means of water, the liquid acquires after some time a violet colour so intense that it appears almost black and opaque. If the treatment with chlorine is prolonged, and the cooling insufficient, a reduction takes place, and manganous chloride gradually separates. The mixture should be shaken frequently, and kept from much light. If the dark liquid is poured off, a substance is obtained partly soluble in ether with intense violet colour; the insoluble residue is unchanged manganese oxide. The ether poured off, gives after some hours an abundant separation of manganous chloride, and loses its colour. When strong hydrochloric acid (sp. gr. 1·19) is shaken with absolute ether, two layers are obtained, the lower, a solution of ether in hydrochloric acid, and the upper, a solution of hydrochloric acid in ether. When these are treated separately with manganese peroxide, the ethereal hydrochloric acid solution acquires a green, whilst the hydrochloric acid containing ether acquires a violet colour. Hence the colour appears to depend on the amount of water present (comp. Nicklès, *Ann. Chim. Phys.* [4], **5**, 161).

A number of experiments are described which were made to determine the valency of the manganese in the compounds obtained by the action of hydrochloric acid on manganese peroxide. The result points to the formula Mn_2Cl_6. When the reaction takes place at 10°, more chlorine is taken up, and it is probable that the compound $MnCl_4$ is formed.

Manganese sesquioxide, Mn_2O_3, yielded the same chloride, Mn_2Cl_6, when treated with ether containing hydrochloric acid.

Manganese fluoride, $Mn_2F_6 + 6H_2O$, is obtained in the pure state by dissolving artificial manganese peroxide in hydrofluoric acid; the product is filtered through spongy platinum, evaporated down and kept over sulphuric acid.

Manganese potassium fluoride, $4KF,Mn_2F_6 + 2H_2O$, is prepared by treating manganous hydroxide (Otto, *Annalen*, **93**, 372) with pure dilute hydrofluoric acid; the product is filtered and treated with excess of potassium fluoride, when a rose-coloured, crystalline precipitate is formed. This is washed with water containing hydrofluoric acid, and dried on platinum. It is decomposed by water at the ordinary temperature. Hydrochloric acid decomposes it with a dark colour; when the solution is treated with water, the solution becomes transparent and bright yellowish-red. The salt dissolves in sulphuric acid, yielding an amethyst-coloured liquid, which becomes red on the addition of water. The solution in phosphoric acid is red. The salt is identical with the one to which Nicklès (*Compt. rend.* **65**, 107) ascribed the formula $2KF,MnF_4$. The salt, $2KF,MnOF_2$, is obtained by adding manganese tetrachloride to a boiling solution of potassium fluoride; it is probably identical with Nicklès' salt, $4KF,Mn_2OF_4$.

The salt, $4KF,Mn_2F_6 + 2H_2O$, was also prepared by heating manganese peroxide with hydrogen potassium fluoride, and by precipitation from a solution of potassium fluoride with a solution of manganese peroxide in hydrofluoric acid. N. H. M.

Action of Potassium Permanganate on Sodium Thiosulphate. By M. Gläser (*Monatsh. Chem.*, **7**, 651—654).—According to Hönig and Zatzek (Abstr., 1886, 504), a boiling neutral solution of sodium thiosulphate is not completely oxidised to sulphate by potassium permanganate. Experiments in which sodium thiosulphate was boiled with solutions of permanganate, show that when 1 c.c. of the solution contains 0·007487 gram of permanganate, and the boiling is continued for 15 to 20 minutes, 1·98 to 2·69 per cent. of the thiosulphate is not oxidised to sulphate, whilst when concentrated solution of permanganate is employed, the oxidation is complete. In alkaline solution, and at the ordinary temperature, the oxidation is almost, but not quite, complete.

The compound manganite formed in the reaction is stable, and is not decomposed by cold or hot water. Numerous analyses confirm the formula $KH_3Mn_4O_{10}$, previously assigned to it. The author adheres to the equation previously suggested by him (Abstr., 1885, 957), and considers that it holds good whether the reaction takes place in the boiling concentrated solution of permanganate or in a more dilute solution. N. H. M.

Compounds of Stannic Oxide. By A. Ditte (*Compt. rend.*, **104**, 172—175).—Stannic hydrate, produced by the action of alkalis on a solution of stannic chloride, dissolves readily in warm dilute sulphuric acid (1 : 8), forming a limpid solution, which when concentrated until it contains not more than 3 or 4 vols. of water to 1 vol. of sulphuric acid, deposits at first colourless, radiating needles, then rhomboïdal lamellæ, and eventually hexagonal prisms with two parallel faces largely developed. All the crystals have the composition $SnO_2,2H_2SO_4$.

The same compound is obtained by the action of sulphuric acid

of suitable concentration on the hard, vitreous hydrate $SnO_2,2H_2O$, obtained by dissolving gelatinous stannic hydrate in ammonia, and evaporating the liquid; on metastannic acid obtained by treating the metal by nitric acid; and on strongly heated anhydrous stannic oxide. In the last case the rate of solution is very slow. The form of the crystals varies in the manner already described with the relative proportions of acid and water in the liquid.

The crystals are decomposed by water, but the stannic oxide is kept in solution by the sulphuric acid which is liberated, and a precipitate is only obtained when water is added in such quantity that the liquid does not contain more than about 43 grams of sulphuric acid per litre. The crystals are very deliquescent, and form a colourless, transparent liquid when exposed to the air; this solution does not crystallise on evaporation, but forms a hard, vitreous mass. If, however, some sulphuric acid is added to the liquid, crystals of $SnO_2,2H_2SO_4$ are readily obtained. They dissolve readily in dilute sulphuric acid, especially on heating, are not affected by ether, but are decomposed by alcohol with removal of sulphuric acid.

If the sulphuric acid is not in large excess, but has dissolved a considerable proportion of stannic oxide, it forms a transparent jelly on cooling, which is sometimes opalescent. This liquefies when heated, but gelatinises again when cooled. The jelly is strongly acid, and does not become crystalline even after several weeks. If, however, it is mixed with an excess of ether, it yields a precipitate of slender, white needles of the compound SnO_2,H_2SO_4. This compound dissolves in cold water, and the solution is at first limpid, but soon becomes turbid, owing to the separation of gelatinous stannic hydrate.

A compound of the same kind containing selenic acid is readily obtained by dissolving gelatinous stannic oxide in a warm solution of selenic acid, and evaporating to a syrup. When the liquid is cooled, it deposits transparent rhomboïdal lamellæ or hexagonal prisms of the composition SnO_2,H_2SeO_4. These crystals are hygroscopic, and are decomposed by excess of water, with separation of stannic hydrate. This compound is formed even in presence of a large excess of selenic acid.

Titanic and zirconic oxides yield similar products. C. H. B.

Titanium. Part II. By O. v. d. Pfordten (*Annalen*, **237**, 201—235).—The yellow colour of titanium tetrachloride is due to the presence of vanadium oxychloride. This impurity may be removed by treatment with sodium amalgam. The pure chloride is a colourless liquid boiling between 135° and 136°. It is not decomposed by dry oxygen, but fumes in moist air. Titanium tetrachloride is miscible with alcohol, and on the addition of water the solution remains clear. A yellow precipitate is formed when the chloride is poured into hydrochloric acid; it is soluble in an excess of acid. Titanium chloride does not conduct electricity.

A gelatinous modification of hydrated titanic oxide is occasionally obtained by fusing titanium dioxide with potassium carbonate, and adding hydrochloric acid to the aqueous solution of the product. When sodium amalgam is left in contact with titanium tetrachloride,

a black deposit of the dichloride or a violet deposit of the trichloride is slowly formed on the surface of the amalgam.

The dichloride dissolves in water and in alcohol with a brown coloration, but it is insoluble in ether. On exposure to the air, the aqueous solution deposits titanic acid; the alcoholic solution remains clear, but contains organic chlorine products. With potassium thiocyanate and ether, titanium dichloride exhibits a delicate and characteristic reaction; the ether acquires a dark-brown colour. Robinson and Hutchings (*Amer. Chem. J.*, **6**, 74) describe a method of preparing metallic titanium by the action of sodium on titanic chloride in sealed tubes at 130°. The author finds that this reaction yields a considerable quantity of titanium dichloride, but little if any metallic titanium.

Titanium trichloride mixed with dichloride is precipitated when sodium amalgam is added to a solution of the tetrachloride in hydrochloric acid. The powder dissolves in water, forming a violet solution. When sodium amalgam acts on a solution of potassium titanofluoride and hydrochloric acid, a green solution is produced which does not contain any dichloride. On the further addition of sodium amalgam, the solution becomes colourless, and finally deposits a black precipitate of $Ti(OH)_2$. If the solution contains only a small quantity of acid, the sesquioxide is precipitated.

The three chlorides exhibit the following reactions:—

Soluble in	$TiCl_2$.	$TiCl_3$.	$TiCl_4$.
Water or alcohol...	readily (brown)	readily (violet or green)	readily (colourless)
Ether	insoluble	insoluble	,, (yellow)
Hydrochloric acid ..	sparingly	sparingly	freely

	TiO_2. Mixture of $TiCl_4$ and alcohol diluted with water.	Ti_2O_3. Violet solution from $TiCl_4$ or green solution from K_2TiF_6 in hydrochloric acid.	TiO. Aqueous solution.
Ether reaction	—	—	brown.
Ammonia	white	bluish-black	black.
Sodium phosphate..	white	bluish-white	bluish-black.
,, oxalate	white	yellow-brown solution	green-brown solution in excess.
,, acetate	white	—	green-black.
K_4FeCy_6	reddish-yellow	brownish-red	dark-brown.
K_3FeCy_6	yellow	coffee	red-brown.
Tannic acid.....	orange	brown solution	reddish-brown solution.

Titanium sesquioxide is not formed as Ebelmann states (*Ann. Chim. Phys.* [3], **20**, 394) by the action of hydrogen on titanium dioxide at a red heat. The product has the composition of Ti_7O_{12}. W. C. W.

Vanadates of the Alkaline Earths. By O. Manasse (*Chem. Centr.*, 1886, 773—774).—The *normal barium salt*, $BaV_2O_6 + H_2O$, is obtained by adding barium chloride to a solution of the normal potassium salt. Precipitated from the acid potassium salt, it is often obtained as a yellowish-white powder mixed with orange-red crystals. An *acid barium salt*, $Ba_3V_{10}O_{28} + 19H_2O$, is formed by precipitating the acid potassium salt with a soluble barium salt. The precipitate first formed slowly changes into red-yellow crystals, mixed with the yellowish-white powder of the preceding salt, the solution gradually becomes quite colourless. It is soluble in water to the extent of 1 in 5000. The salt is obtained in beautiful, red, prismatic crystals, when equivalent amounts of potassium divanadate and barium chloride are mixed with a large excess of acetic acid. *Barium orthovanadate*, $Ba_6V_2O_8$, cannot be obtained, owing to its great instability; it is decomposed into barium pyrovanadate and barium hydroxide at the time of its formation.

Strontium Salts.—The *normal* salt, $SrV_2O_6 + 4H_2O$, is described, and also *acid* salts, having the composition $Sr_3V_8O_{23} + 14H_2O$, $Sr_5V_{14}O_{39} + 30H_2O$, and $SrV_8O_{21} + 11H_2O$. When potassium divanadate and strontium chloride are allowed to crystallise together, the following double salts are obtained:—α and β, $K_8V_{14}O_{39} + 20H_2O + 3(Sr_4V_{14}O_{39} + 20H_2O)$; $3(Sr_4V_{14}O_{39} + 30H_2O) + K_8V_{14}O_{39} + 30H_2O$; and a γ-salt, $K_8V_{14}O_{39} + 18H_2O + Sr_4V_{14}O_{39} + 18H_2O$, and also $K_4V_{10}O_{27} + 12H_2O$.

Calcium Salts.—The *normal* salt, $CaV_2O_6 + 4H_2O$, is obtained by allowing a mixture of normal potassium vanadate and calcium chloride to evaporate. The *acid* salt, $Ca_3V_8O_{23} + 15H_2O$, is formed when equivalent amounts of potassium divanadate and calcium chloride are mixed with excess of acetic acid. The *tetravanadate*, $CaV_4O_{11} + 6H_2O$, is obtained in red crystals by evaporating potassium divanadate and calcium chloride. Other salts prepared were:—$Ca_3V_{14}O_{39} + 7H_2O$, $Ca_3V_{16}O_{43} + 26H_2O$, and $CaV_4O_{11} + 4K_2V_4O_{11} + 22H_2O$, potassium calcium tetravanadate.

Magnesium Salts.—The *normal* salt, $MgV_2O_6 + 6H_2O$, is prepared by boiling finely powdered vanadic acid with excess of magnesium carbonate. *Acid* salts, $2(Mg_2V_6O_{17}) + 19H_2O$ and $Mg_3V_{10}O_{28} + 28H_2O$, were also prepared.

When a few drops of nitric or sulphuric acid is added to these salts, a hydrate of vanadic acid, $H_2V_2O_6$, is formed, which is much more soluble than the crystallised vanadic acid.

The author determined the vanadic acid in the above salts by reducing the acid and titrating with permanganate. He found that the reduction of vanadic acid is best effected by hydrogen sulphide, or by sulphurous anhydride with a simultaneous passage of carbonic anhydride.

A compound, V_8O_{17}, was obtained as a dark blue or black powder with metallic lustre, by dissolving vanadic acid containing oxide in potassium hydroxide. It can be regarded as a mixture of $V_2O_5 + 3V_2O_4$, or of $V_4O_9 + 2V_2O_4$. G. H. M.

Valency of Bismuth. By A. Michaelis (*Ber.*, **20**, 52—54).—See this vol., p. 368.

Action of Hydrogen Peroxide on Bismuth Salts. By K. Hasebroek (*Ber.*, **20**, 213—218).—When commercial (3 per cent.) hydrogen peroxide, rendered alkaline with ammonia (or potash), is added to a bismuth salt and the mixture gently warmed, evolution of oxygen occurs and a characteristic orange-yellow precipitate of bismuth pentoxide is formed; the reaction is of such delicacy that 1 part of bismuth in 100,000 can be detected by its means. To obtain the pentoxide in the pure state, it is necessary to work in an atmosphere free from carbonic anhydride, otherwise absorption of the gas and formation of bismuthyl carbonate takes place. The air-dried bismuth pentoxide contains less water than corresponds with 1 mol. H_2O; it is a bright orange-yellow, amorphous powder, insoluble in water and alkalis, but soluble in dilute acids, solutions of varying shades of red being formed when dilute nitric and sulphuric acids are used as solvents. When heated with alkalis or alone, it becomes brown, and by further heating melts to form crystalline bismuth trioxide. Treated with hydrochloric and sulphuric acids, it evolves chlorine and oxygen respectively, whilst hydrogen peroxide is readily decomposed by it. W. P. W.

Atomic Weight of Gold. By G. Krüss (*Ber.*, **20**, 205—210).—The collective results obtained in a determination of the atomic weight of gold are given. Two salts were employed, the neutral auric chloride, $AuCl_3$ (in solution), and potassium gold bromide, $KAuBr_4$. The gold chloride was obtained by passing chlorine over finely divided gold; to remove excess of chlorine, the product was exposed for a day to air dried by passage over sulphuric acid and phosphorus pentoxide, then allowed to remain for several weeks over frequently renewed soda-lime, and finally decomposed by water into a solution of neutral auric chloride. The potassium gold bromide was prepared by adding finely divided gold to potassium bromide and bromine in aqueous solution; the salt is anhydrous and only very slightly hygroscopic.

Number of experiments made with each method.	Ratio determined.		Atomic weight.	Difference between the maximum and minimum values found.
8	Solution of neutral auric chloride ...	$Au : Cl_3$	196·622	0·101
4	Potassium gold bromide	$Au : Br_3$	196·619	0·110
4	Ditto	$Au : KBr$	196·620	0·134
5	Ditto	$Au : Br_4$	196·743	0·225
9	Ditto	$Au : KBr,Br_3$	196·741	0·306
30		Mean	196·669	0·175

The values found for the atomic weight (O = 15·96) are given in the table (p. 340).

The author adopts the value 196·64 as that of the atomic weight of gold. W. P. W

Sublimed Auric Chloride. By G. Krüss (*Ber.*, **20**, 211—213).—When a continuous current of dry chlorine is passed over powdered gold, and the temperature gradually raised, it is found that at 140° a small quantity of reddish-brown vapour is formed which condenses to a yellowish-red sublimate; if the temperature is kept constant the sublimation soon ceases, and the gold is entirely converted into aurous auric chloride. When the temperature is raised to 180—190° this compound decomposes, chlorine is evolved, and green aurous chloride and a small quantity of volatile gold chloride are formed. At 220—230° a small quantity of gold chloride again volatilises, whilst the aurous chloride decomposes into gold and chlorine, and at 300° the gold, contrary to Debray's statement (*Compt. rend.*, **69**, 985), remains unaltered in the current of chlorine. On allowing the temperature to fall these changes take place in the reverse order. The amount of volatile gold chloride, which analysis shows to be auric chloride, $AuCl_3$, and not a higher chloride as stated by Prat (*Compt. rend.*, **70**, 840), is very small; thus, 100 repetitions of the process with a layer of powdered gold 30—35 cm. long, yielded less than 0·12 gram of auric chloride in the form of a sublimate consisting of lustrous, reddish-brown needles. W. P. W.

Mineralogical Chemistry.

Amorphous Carbon (Graphitoïd) in the Saxon Erzgebirge. By A. Sauer (*Zeit. Kryst. Min.*, **12**, 527).—Amorphous carbon is widely distributed throughout the mica schists and phillites of the Erzgebirge. It is not identical with graphite or with anthracite. The author finds that it is identical with the amorphous carbon described by Inostranzeff (Abstr., 1881, 357), and suggests for the substance the name of graphitoïd. The analysis gave the following results:—

Ash.	C.	H_2O.	H.	Total.
73·85	24·85	1·01	0·06	99·77

B. H. B.

Crystallisation of Native Copper. By E. S. Dana (*Amer. J. Sci.*, **32**, 413—429).—This elaborate memoir is based on a careful study of the beautiful collection of 60 specimens of native copper from Lake Superior, in the possession of Mr. C. S. Bement. The author also had the use of a large number of specimens belonging to the cabinets of Professor G. J. Brush, and of the Yale College

Museum. The paper is accompanied by illustrations of 54 varieties of crystalline forms of native copper. The planes observed by the author are : $\infty O\infty$, ∞O, O, $\infty O4$, $\infty O\frac{5}{2}$, $\infty O2$, $\infty O\frac{5}{3}$, 303, 202, $\frac{1}{5}8O\frac{2}{5}$, $110\frac{11}{6}$, 604. Of these, the trisoctahedron 202, and the hexoctahedra $110\frac{11}{6}$ and 604, are new to the species. B. H. B.

Crystallographic Notes. By W. G. Brown (*Amer. J. Sci.*, **32**, 377—380).—1. *Artificial Copper Crystals.*—In a cell of a Calland gravity battery which had remained undisturbed for three months, there was found attached to the insulating wire coming from the copper plate, at the point where it passed the zinc plate, a pendant mass consisting almost entirely of copper crystals. The crystals were evidently accidentally formed by electrolysis. The upper part of the mass consists of spongy dendritic copper, whilst the lower and larger portion consists of definite copper crystals. By far the greater number of the crystals are twins, either according to the spinel law, twinning plane an octahedral face, or the twinning plane is that of a trapezohedron forming polysynthetic twins.

2. *Artificial Crystallised Cuprite.*—On the outside of the spongy portion of the copper described above, there is a purple layer of crystals of cuprous oxide. Individually, they are of a dark ruby-red colour; the forms present being combinations of the octahedron and cube. Another example of crystallised cuprous oxide was found on a German-silver camp spoon picked up on the site of a magazine constructed in 1863, on Morris Island, South Carolina. The short time in which the crystals have formed seems a noteworthy feature of this occurrence. The spoon could not have been exposed more than 20 years.

3. *Crystallised Cerussite.*—At Morris Island, among the *débris* of a battle-field, a dozen Minié balls were picked up. Upon various parts of the surface of these were patches of lead carbonate, sometimes amorphous and sometimes acicular. The balls had not been fired. It is possible that the formation of the carbonate was hastened by the rapid oxidation of the lead by the nitre of the gunpowder of the cartridge in the presence of moisture. B. H. B.

Mineralogical Notes. By A. Genth (*Zeit. Kryst. Min.*, **12**, 487—492).—The author gives descriptions and analyses of the following minerals:—1. Native tin from the Aberfoil River, New South Wales; 2. Joseite and tetradymite from San José, Minas Geraes; 3. Galenobismuthite containing selenium from Falun, Sweden; 4. Silver bismuth glance from Lake City, Colorado; 5. Cosalite from the Alaska and Gladiator mines in Ouray Co., Colorada; 6. Beegerite from the Treasury Vault mine, Summit Co., Colorado; 7. Fahlerz from the Governor Pitkin mine, Lake City, Colorada; 8. Polybasite from the Terrible Lode mine, Clear Creek Co., Colorado; 9. Arsenical pyrites from North Alabama; 10. Brucite from Berks Co., Pennsylvania; 11. Ilmenite and oligoclase from the Carter mine, North Carolina; 12. Topaz from Stoneham, Maine; 13. Orthoclase from French Creek, Chester Co., Pennsylvania; 14. Muscovite pseudomorphs after nepheline from Wakefield in Canada; 15. Stilp-

nomelane from Antwerp, New York; 16. Calamine from the Bertha mine, Pulaski Co., Virginia; 17. Titanite from Statesville, North Carolina; 18. Vanadinite from Wanlockhead, Scotland; 19. Annabergite from the Gem mine, Silver Cliff, Colorado. B. H. B.

Mineralogical Notes. By E. S. Dana (*Amer. J. Sci.*, **32**, 386—390).—The author gives the results of a crystallographical investigation of the following minerals:—

1. *Columbite* from Standish, Maine.—The results of the author's examination of this mineral have already been published (this vol., . 20).

2. *Diaspore* from Newlin, Pennsylvania.—The crystal examined is the finest ever found at the locality. It is prismatic in habit and showed the following planes:—$\infty P\breve{\infty}$, $\infty P\breve{2}$, $\infty P2$, $\infty P\breve{5}$, and $\frac{3}{2}P\frac{5}{2}$; the last pyramid being new to the species. On crystals of diaspore from Chester, Massachusetts, the author has observed the planes $1P\frac{4}{3}$ and $1P\breve{2}$, new to the species.

3. *Zincite.* — The knowledge of the crystals of zinc oxide has hitherto rested on observations of artificial crystals, the native mineral showing usually only massive forms. The cabinet of Mr. C. S. Bement contains several specimens of zincite from Stirling Hill, New Jersey, showing distinct crystals. The angles measured show a fair agreement with the angles of the artificial forms.

4. *Sulphur.*—A specimen of native sulphur from Rabbit Hollow, in the cabinet of Professor Brush, is interesting on account of the complexity of its form. Fifteen planes were observed; of these $\frac{3}{5}P\overline{3}$ and $\frac{1}{4}P$ are new to the species. B. H. B.

Copper Mineral from Sunnerskog, Sweden. By G. Lindström (*Zeit. Kryst. Min.*, **12**, 512—513).—The mineral is dark indigo-blue, with a blue streak and faint metallic lustre. Analysis gave the following results:—

Cu.	S.	Fe_2O_3.	CaO.	Insol.	Total.
74·29	24·22	0·10	0·59	0·51	99·71

A mineral analysed by Hahn, and named carmenite, had the same composition. It was, however, regarded by Dana as an impure copper glance, mixed with covelline. B. H. B.

Galenobismuthite containing Selenium from the Falun Mine. By M. Weibull (*Zeit. Kryst. Min.*, **12**, 511—512).—Galenobismuthite containing selenium was first observed in the quartz at the Falun Mine in Sweden. Its occurrence is of practical importance, as it has been proved that the native gold is always accompanied by this mineral at Falun. The mineral has a perfect cleavage; H. = 3. Thin plates are flexible, but scarcely elastic. The colour is a steel grey; sp. gr. 6·97. Analysis gave the following results:—

Bi.	Pb.	Cu.	Fe.	S.	Se.	Total.
49·73	24·62	0·77	0·61	9·82	13·61	99·66

The formula is thus $PbS,Bi_2S_3 + PbS,Bi_2Se_3$. The mineral is

probably isomorphous, with the lead-bismuth glance described by H. Sjögren.

This mineral has also been analysed by A. Genth (*Zeit. Kryst. Min.*, **12**, 487—488), the mean of five analyses giving the following results, after 3·96 to 8·8 per cent. of impurities had been subtracted :—

Bi.	Pb.	Ag.	S.	Se.	Total.
49·88	27·88	0·33	9·75	12·43	100·27

B. H. B.

Emmonsite, an Iron Telluride. By W. F. Hillebrand (*Zeit. Kryst. Min.*, **12**, 492—493).—This new mineral from Colorado occurs in yellowish-green scales in a hard brown, vein-mass, consisting of lead carbonate, quartz, and a brown substance containing iron and tellurium. The mineral is probably monosymmetric. The quantity of mineral available for analysis was very small. Three analyses of the brown substance gave the results under I, II, III; an analysis of the green particles carefully picked out, but still not pure, gave the results under IV. The mean results, probably the most correct, are given under V, 0·53 per cent. of selenium having been subtracted :—

	I.	II.	III.	IV.	V.
Te(Se)	59·77	59·15	59·05	59·14	58·75
Fe	14·00	14·06	14·90	14·20	14·29

In Analysis I, 3·28 per cent. of water was found, and in Analysis IV 1·94 of ZnO and 0·56 of CaO. The mineral is a ferri-telluride. It has been named in honour of Mr. S. J. Emmons, of the U.S. Geological Survey. B. H. B.

Elpasolite, a New Mineral. By W. J. Cross and W. J. Hillebrand (*Zeit. Kryst. Min.*, **12**, 495).—This is a new Colorado mineral, named after the county (El Paso) in which it was found. It occurs in cavities in massive pachnolite, in the form of compact masses, on which are planted indistinct, isometric crystals. Analysis gave the following results :—

Al.	Ca.	Mg.	K.	Na.	F.	Total.
11·32	0·72	0·22	28·94	9·90	(46·98)	98·08

The determination of the alkalis is only an approximation, and the fluorine is calculated on the assumption that it is completely combined with metals. It is suggested that the mineral should be regarded as a cryolite, in which two-thirds of the potassium is replaced by sodium. B. H. B.

Gearksutite from Ivigtut, Greenland. By A. E. Nordenskiöld (*Zeit. Kryst. Min.*, **12**, 513—514).—The mineral is, according to the author, of recent formation, being due to the action of calcareous water on the water circulating in the fissures of the cryolite deposit. Analysis gave results identical with those obtained by Cross and Hillebrand (Abstr., 1884, 21), the formula being $CaF_2 + (AlF_3)(AlH_3O_3) + H_2O$. B. H. B.

Chemical Composition of Ralstonite. By S. L. Penfield and D. N. Harper (*Amer. J. Sci.*, **32**, 380—385).—Analyses of the rare mineral ralstonite have been published by Nordenskiöld, Penfield, and Brandt. The authors have now made an analysis of a specimen of ralstonite associated with thomsenolite from Arksut Fjord, Greenland, the results being as follows:—

Mg.	Na.	K.	Ca.	Al.	F.	H_2O.	Total.
4·39	4·27	0·12	0·03	24·25	39·91	18·73	91·70

The ratio of $(MgNa_2K_2) : Al = 1 : 3$ nearly. This ratio being assumed to be correct, the ratio of the fluorine necessary to unite with the metals should be 11, whereas only 7·56 was found. The assumption that hydroxyl replaces fluorine not only makes up for the deficiency in the analysis, but also leads to a very satisfactory ratio. The assumption is also well supported by actual experiment. Using the actual water of crystallisation and hydroxyl determinations, and determining the fluorine by difference, the latter part of the analysis would be as follows:—

F.	OH.	H_2O.
40·79	15·78	10·37

Assuming these conclusions to be correct, the mineral is an isomorphous mixture of $(MgNa_2)Al_3F_{11},2H_2O$ and $(MgNa_2)Al_3(OH)_{11} + 2H_2O$. B. H. B.

Brucite from the Ural. By A. A. Lösch (*Zeit. Kryst. Min.*, **12**, 514).—The mineral occurs with chlorite, calcite, perowskite, forsterite, and waluewite at the Nikolaje-Maximilianoffski Mine; sp. gr. = 2·388. Analysis gave the following results:—

MgO.	FeO.	H_2O.	CO_2.	Total.
69·03	0·76	30·15	0·09	100·03

B. H. B.

Artificial Production of Zincite and Willemite. By A. Gorgeu (*Compt. rend.*, **104**, 120—123).—When zinc sulphate is gradually heated to bright redness, it yields zinc oxide in small crystals which are more readily obtained if the zinc salt is mixed with an equivalent quantity of an alkaline sulphate. Decomposition is then less rapid and the crystals separate in the fused mass. Before decomposition is complete, the product is cooled and extracted with water, when zinc oxide is left in heavy, transparent, nacreous, greenish-yellow or greenish, hexagonal prisms which, like the crystals of zincite, belong to the hexagonal system. In hardness and sp. gr. (5·5) the artificial crystals are identical with the natural oxide. Zinc nitrate also yields good crystals if only heated to partial decomposition, and the crystals are also obtained by heating equal parts of zinc fluoride and potassium fluoride in presence of aqueous vapour.

Willemite, $SiO_2,2ZnO$, is obtained when an intimate mixture of zinc sulphate with 0·5—1 equivalent of an alkaline sulphate and one-thirtieth of their weight of hydrated silica is heated for an hour

at a temperature sufficient to cause a slight but regular evolution of sulphurous anhydride. The fused mass is treated with water, which leaves a residue of tridymite and basic zinc sulphate with strongly birefractive crystals of willemite, which form hexagonal prisms with obtuse rhombohedral terminations. In hardness (5·5), sp. gr. (4·25), and general properties, the artificial crystals are identical with those of the natural mineral. Calcined silica and sand will give the same results, but the action is much slower.

No acid zinc silicate was obtained even with an excess of silica.

When a mixture of zinc chloride and an alkaline chloride with silica is heated in presence of water-vapour, crystals of the composition $SiO_2,2ZnO$, are obtained, but their exact form could not be determined. C. H. B.

Goslarite from Montana. By R. Pearce (*Zeit. Kryst. Min.*, **12**, 494).—Goslarite occurs in long, acicular crystals in some old workings, 400 feet deep, in the Gagnon Mine, Butte City, Montana. Analysis gave the following results:—

SO_3.	ZnO.	CuO.	MnO,FeO.	H_2O.	Total.
28·09	(27·56)	0·12	0·30	43·93	100·00

B. H. B.

Place of Spodiosite in the Mineral System. By A. Sjögren (*Zeit. Kryst. Min.*, **12**, 512).—In consequence of the chemical and crystallographical resemblance between spodiosite and kjerulfine, the author suggests that the two minerals may be isomorphous compounds, thus:—

Kjerulfine ..... $Mg_2F\cdot PO_4$
Spodiosite ..... $Ca_2F\cdot PO_4$.

The planes of spodiosite calculated from the axial ratio of kjerulfine would be ∞P, $\infty P\infty$, $-2P$, $+2P$, $4P\infty$. B. H. B.

Sarkinite, a New Manganese Arsenate. By A. Sjögren (*Zeit. Kryst. Min.*, **12**, 514).—This mineral occurs in veins of white calcite at Pajsberg, in Sweden. It has a greasy lustre, and is of a bright flesh colour, hence its name, from *σάρκινος*, *fleshy*. H. = 4 to 5. Sp. gr. = 4·14 to 4·15. The mineral is brittle, giving a bright red powder. On heating, the powder becomes first grey, then black, and, when strongly ignited, a brownish-black. The crystalline system is unknown, probably monosymmetric. The mean of two analyses gives the following figures:—

As_2O_5.	P_2O_5.	CO_2.	MnO.	FeO.	CaO.	MgO.
41·60	0·21	0·76	51·60	0·13	1·40	0·98

PbO.	H_2O.	Insol.	Total.
0·25	3·06	0·38	100·37

B. H. B.

Polyarsenite, a New Mineral. By L. J. Igelström (*Zeit. Kryst. Min.*, **12**, 515).—The mineral was found at the Sjö mine, in the parish of Grythytta, Örebro, Sweden. It is a hydrated manganese

arsenate, of a reddish-yellow colour, translucent, massive, and without distinct cleavage, or crystal planes. It occurs with hæmatostibiite (a manganese antimoniate) in calcite veins in a mass of tephroite. Sp. gr. = 4·085. Analysis gave the following results:—

H_2O.	CO_2.	As_2O_5.	Sb_2O_5.	MnO.	FeO.	CaO.	MgO.	Total.
3·15	3·51	39·23	1·37	49·88	trace	2·85	0·77	100·76

Formula: $(MnO)_4As_2O_5 + H_2O$. B. H. B.

Crystallised Vanadinite from Arizona and New Mexico. By S. L. Penfield (*Amer. J. Sci.*, **32**, 441—443).—The crystals of vanadinite from Pinal Co., Arizona, are small, seldom over 1 mm. in length, of a deep red colour, and usually show the very simple combinations mentioned by W. P. Blake (*Amer. J. Sci.*, **22**, 410). A few highly modified crystals were found possessing pyramidal hemihedral forms, which are of interest because these forms have rarely been observed in this species. From the best measurements, the axial ratio $a : c = 1 : 0·71121$ was obtained. This agrees closely with the ratios given by Schabus, 1 : 0·71157, and by Vrba, 1 : 0·7112177. The measured angles agree closely with those calculated from the axial ratio. The crystals contain but a trace of As_2O_5.

The crystals from the Sierra Grand Mine, Lake Valley, New Mexico, are straw-yellow in colour. The crystals give distinct V_2O_5 and As_2O_5 reactions, thus corresponding exactly with the description given by F. A. Genth and G. vom Rath of the species named by them *endlichite*. The axial ratio was found to be $a : c = 1 : 0·7495$. The measured angles do not agree well with those calculated from the axial ratio. The presence of As_2O_5 in the mineral must therefore tend to increase the length of the vertical axis. B. H. B.

Columbite from Colorado. By W. P. Headden (*Zeit. Kryst. Min.*, **12**, 494).—A mineral, hitherto regarded as tin ore, from Turkey Creek, Jefferson Co., Colorado, is found to be columbite rich in manganese. Sp. gr. 5·48. Analysis gave the following results:—

Nb_2O_5.	$WO_3 + SnO_2$.	FeO.	MnO.	Total.
77·83	1·00	9·92	11·23	99·98

B. H. B.

Phosphoric Anhydride in Felspar. By G. Lindström (*Zeit. Kryst. Min.*, **12**, 513).—The author gives two analyses of felspar from Tammela and Skogböle in Finland. They present nothing worthy of note, with the exception of the phosphoric anhydride found by the author. In one case the percentage is 0·72, and in the other 0·58. Thin sections of the mineral analysed were found to contain a small quantity of apatite. The author is, however, of opinion that the phosphoric anhydride must also be present in some other less soluble compound. B. H. B.

Lithia Micas. By F. W. Clarke (*Amer. J. Sci.*, **32**, 353—361).

1. *The Lepidolites of Maine.*—In the western part of Maine, there are

a series of veins of albitic granite containing lithia mica and coloured tourmalines. The localities, in the towns of Rumford, Paris, Norway, Hebron, and Auburn, are all within a narrow belt of 40 miles in length. Analyses of the lepidolite gave the following results:—

	1. Purple. Rumford.	2. Foliated. Paris.	3. Granular. Hebron.	4. Border. Auburn.	5. Granular. Auburn.	6. White. Norway.	7. Brown. Norway.
SiO_2	51·52	50·92	48·80	49·62	51·11	49·52	50·17
Al_2O_3	25·96	24·99	28·30	27·30	25·26	28·80	25·40
Fe_2O_3	0·31	0·30	0·29	0·31	0·20	0·40	0·87
FeO	undet.	0·23	0·09	0·07	0·07	0·24	0·45
MnO	0·20	trace	0·08	0·55	0·17	0·07	0·23
CaO	0·16	trace	0·10	—	0·12	0·13	undet.
MgO	0·02	trace	0·07	—	0·01	0·02	undet.
Li_2O	4·90	4·20	4·49	4·34	4·98	3·87	4·03
Na_2O	1·06	2·11	0·74	2·17	1·43	0·13	} 13·40
$(K,Rb,Cs)_2O$..	11·01	11·38	12·21	11·19	12·25	12·63	
H_2O	0·95	1·96	1·73	1·52	0·94	1·72	2·02
F	5·80	6·29	4·96	5·45	6·57	5·18	5·05
Total	101·89	102·38	101·86	102·52	103·11	102·71	101·62
Less oxygen ..	2·44	2·64	2·02	2·29	2·76	2·18	2·13
Total	99·45	99·74	99·84	100·23	100·35	100·53	99·49

As regards cæsium and rubidium, the Maine lepidolites offer some points of difference. With specimens 3, 4, 5, and 6 approximate estimations were made with the following results:—

	3.	4.	5.	6.
K_2O	11·44	8·03	10·51	8·82
Rb_2O }	0·77	{ 2·44	1·29	3·73
Cs_2O }		{ 0·72	0·45	0·08
Total	12·21	11·19	12·25	12·63

The foregoing analyses of several distinct types of lepidolite from five distinct localities indicate a great consistency of composition. In most of the analyses, the water and fluorine appear to vary reciprocally, suggesting the ordinary replacement of the latter element by hydroxyl. With this assumption, the formula for lepidolite may be written $Al_2LiKF_2Si_3O_9$; a formula generally accepted, but which now rests upon the basis of a wider range of analytical data.

2. *The Iron-lithia Micas of Cape Ann, Massachusetts.*—Cryophyllite, a remarkable mica from this locality, was described by Cooke in 1867 (*Amer. J. Sci.*, **43**, 217), who also analysed an associated lepidomelane, to which Dana afterwards gave the name of annite. The cryophyllite varies considerably in external character, and three well-marked types of it were analysed. They may be described as follows:—I, broadly-foliated, brilliant, blackish-green; II, paler, dull-green, less lustrous, apparently altered; III, an aggregation of minute, hexagonal pyramids,

dark-green, almost granular in appearance. The analytical results were as follows:—

	I.	II.	III.	IV.
SiO_2	51·96	51·46	52·17	31·96
TiO_2	—	—	—	3·42
Al_2O_3	16·89	16·22	16·39	11·93
Fe_2O_3	2·63	2·21	4·11	8·06
FeO	6·32	7·63	5·99	30·35
MnO	0·24	0·06	0·32	0·21
CaO	0·12	trace	trace	0·23
MgO	0·03	0·17	trace	0·05
Li_2O	4·87	4·81	4·99	trace
Na_2O	0·87	0·89	0·63	1·54
K_2O	10·70	10·65	10·48	8·46
H_2O	1·31	1·12	1·46	4·25
F	6·78	7·44	7·02	trace
Total	102·72	102·66	103·56	100·46
Less oxygen	2·86	3·11	2·95	—
Total	99·86	99·55	100·61	—

The three samples were sensibly identical, and not very different from the material analysed by Cooke. The integrity of the species seems to be clear; and it cannot be identified with zinnwaldite. Empirically, as deduced from the new analyses, the formula may be written $R'_6Al_2F_2(SiO_3)_5$.

With the annite, quite unexpected results were obtained (Analysis IV). The material was black, brilliant, broadly foliated, and seemed to be very pure. The analytical results clearly show that this mica and that analysed by Cooke are entirely distinct, and the question is raised whether the Cape Ann granite may not contain a series of complex isomorphous mixtures. B. H. B.

Lucasite, a New Variety of Vermiculite. By T. M. Chatard (*Amer. J. Sci.*, **32**, 375—377).—A distinct variety of the vermiculite-group has been found among the minerals occurring with corundum at Corundum Hill, North Carolina. The name *lucasite* has been given to it in honour of Dr. H. S. Lucas, well known in connection with corundum mining in the Southern States. The mineral was found in a corundum vein. It is foliated, compact, also disseminated; cleavage, basal; colour, yellowish-brown; lustre, submetallic, somewhat greasy; easily decomposed by concentrated hydrochloric acid, the silicic acid separating in pearly scales. When heated, it gives off much water and exfoliates with considerable force. Under the microscope, it was found to be biaxial and negative, but the angle between the optic axes, as seen in a cleavage plate split off parallel to the base, is uniformly small. On rotating the section, although the cross is plainly distorted into two hyperbolæ, they do not com-

pletely separate from each other. Analysis of the air-dried mineral gave the following results:—

H_2O.	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.
10·76	39·81	12·99	0·54	5·29	0·11	0·05

CaO.	MgO.	K_2O.	Na_2O.	Total.
0·14	24·83	5·76	0·20	100·48

Water determinations gave the following results:—H_2O at 100°, 3·78; H_2O at red heat, 6·98. Total, 10·76. B. H. B.

Lamellar Thomsonite. By A. Lacroix (*Compt. rend.*, **104**, 234—235).—This mineral occurs in a small vein in the labradoric porphyrite at Bishopton, Scotland.

It exists in nacreous, white lamellæ with a rose tint, the ordinary cleavage of thomsonite having become micaceous. These lamellæ are grouped at all angles. The cleavage lamellæ unite parallel with their elongation along the edge (100) (010), and there are also traces of cleavage along (100) and (001). The plane of the optical axes is parallel with (001), and the positive bisectrix is normal to the easy cleavage (010), the maximum birefractive power being 0·027. Under the microscope, the mineral is found to consist of thin plates irregularly superposed like those of zeolites. It has the composition $RO,Al_2O_3,2SiO_2 + H_2O$, R being calcium and sodium, sp. gr. 2·34. When heated before the blowpipe, it yields a white enamel, and it is easily decomposed by hydrochloric acid with gelatinisation.

C. H. B.

White Epidote from the Beagle Canal, Terra del Fuego. By A. Lacroix (*Compt. rend.*, **104**, 235—236).—The mineral forms white needles which cleave parallel with the direction of the elongation. They are monoclinic prisms elongated along the edge (001) (100). The plane of the optical axes is parallel with the face (010), and the positive bisectrix is normal to one face of the zone (001) (100), the separation of the two axes being about 75°, and the maximum birefractive power 0·04. The mineral contains many cavities with liquid enclosures. When heated to redness, it becomes brown, and forms a semi-agglutinated powder, which melts to a brown scoria before the blowpipe. It is scarcely attacked by boiling acids, but gelatinises with hydrochloric acid after being strongly heated.* The mineral has the sp. gr. 3·21 at 5°, and the composition SiO_2, 37·95; Al_2O_3, 30·38; FeO, 7·83; CaO, 20·34; MgO, 0·93; loss on heating 2·64, which agrees with the formula $6RO,4Al_2O_3,9SiO_2$. The high proportion of alumina and the state of oxidation of the iron are especially noteworthy. In external appearance, the mineral strongly resembles zoisite. C. H. B.

Critical Examination of some Minerals. By A. Lacroix (*Compt. rend.*, **104**, 97—99).—*Pterolite*, from the island of Lövö, is

* I have observed the same behaviour in the case of several English specimens of epidote. See Green's *Physical Geology*, p. 128.—C. H. B.

an association of green pyroxene with black mica. The latter is uniaxial and pleochroic, being deep brown along *ng*, and reddish-yellow along *np*. The mineral also contains numerous grains of blue sodalite, rhombohedrons of calcite or dolomite, and intrusions of other minerals. It has no claim to be regarded as a distinct mineralogical species.

Villarsite, from Traverselle, is not a distinct species, but is merely normal peridote cracked in all directions and more or less completely converted into secondary products. In some specimens, the conversion into chrysotile is complete. It resembles serpentine in being a product of the disintegration of olivine.

Grangesite, from Grangesberg, has a composition very similar to that of ripidolite. It forms thin, greenish-brown, isotropic plates, but cannot be regarded as a distinct species.

Gamsigradite, from Gamsigrad, has the optical properties of hornblende, and is pleochroic, being bottle-green along *ng*, greenish-brown along *nm*, brownish-yellow along *np*. The rock in which it occurs is an amphibolic dacite containing labradorite and amphibole.

C. H. B.

Paragonite Schist from the Ural. By A. Arzruni (*Zeit. Kryst. Min.*, **12**, 531).—The author describes a paragonite-schist from the Nizne-Issetsk district, where it occurs interstratified in the chlorite schist. It is filled with inclusions of a colourless, rhombic mineral, which, in its optical characters, is intermediate between zoisite and epidote. In crystalline system, twinning, and cleavage it is identical with zoisite, but in respect of the position of the plane of the optic axes, the character of the double refraction, and the dispersion of the optic axes, it is identical with epidote. B. H. B.

Gaseous Constituents of Meteorites. By G. Ansdell and J. Dewar (*Proc. Roy. Soc.*, **40**, 549—559).—Few analyses have hitherto been made of the gaseous constituents of meteorites, whether of the iron, stony, or carbonaceous classes; the results obtained have shown the presence, in variable proportion, of carbonic oxide and anhydride, hydrogen and methane. The investigation comprises a re-examination of a well-known meteorite, the analysis of several meteoric stones, and an examination of a graphite nodule taken from the interior of an iron meteorite, which is compared with graphites of celestial and terrestrial origin. Analytical results are given of specimens of the Dhurmsala, Pultusk, and Mocs meteorites and of pumice stone. In the former, carbonic anhydride was the largest constituent (about 65 per cent.), whilst marsh-gas in considerable quantity was found in all, and water was evolved, probably in part combined originally in some form, and not entirely absorbed from the atmosphere. A sample of the Dhurmsala meteorite, from which the gases had been removed, was exposed for different periods to a damp atmosphere; water, carbonic oxide and anhydride, and nitrogen were found to be absorbed; the total water given off after this exposure was less than that obtained in the first process of heating.

A sample of celestial graphite was examined and compared with specimens from Borrodale, Siberia, and Ceylon, as also with a partly

decomposed gneiss from Canada; the former gave off about twice as much gas as the latter.

Experiments are quoted to show that this large quantity of gas occluded in celestial graphites cannot be explained by any special absorptive power possessed by the variety of carbon. The hydrogen appears to exist in some combined form, but it is not shown whether the methane is entirely present as such in the meteoritic graphite or is subsequently formed during the heating process.

From the Orgueil meteorite, a typical specimen of the carbonaceous class, sulphur and sulphurous acid, together with ammonium salts, were obtained. V. H. V.

Hot Springs at Wiesbaden. By R. Fresenius (*J. pr. Chem.* [2], **35**, 122—131).—The author makes a full analysis of the solid and gaseous constituents of the water from these springs, and compares it with a similar analysis made in 1849.

The alkaline chlorides and the sulphates have not altered; on the other hand, calcium and magnesium compounds have slightly decreased, whilst silica and iron and manganese oxides have increased. The amount of solid matter delivered yearly by the springs is calculated. H. K. T.

Organic Chemistry.

Derivatives of Erythrene. By E. Grimaux and C. Cloez (*Compt. rend.*, **104**, 118—120).—The hydrocarbon C_4H_6, isolated from the liquid obtained by the compression of coal-gas, yields a tetrabromide crystallising in long, brilliant needles, which melt at 116°, and are almost insoluble in cold alcohol, but dissolve in about 30 times their weight of boiling alcohol of 85°. When heated on a water-bath with alcoholic potash, half the bromine is removed as potassium bromide, and the other product distils over with the alcohol. If water is added to the distillate, an oily liquid separates and rapidly polymerises to a solid, which dissolves only in boiling ethylene bromide. This liquid probably has the composition $C_4H_4Br_2$. If ether is added immediately after precipitation with water, the oily liquid is dissolved and the solution is stable, but if the ether is volatilised, the residue quickly polymerises. When the ethereal solution is mixed with bromine, it yields long, brilliant prisms of the composition $C_4H_4Br_2,Br_4$, which melt at 69°, volatilise in small quantities without decomposition, and are slightly soluble in alcohol, but dissolve readily in ether. The properties of this compound agree with those of the bromide described by Henninger, and it follows that the hydrocarbon obtained from coal-gas is identical with Henninger's erythrene, and is vinyl-acetylene, $CH_2 : CH{\cdot}CH : CH_2$. The name erythrene indicates its relation to erythrol, and may conveniently be retained.

The tetrabromide obtained by Caventou from the hydrocarbons

formed by the pyrogenic decomposition of amyl alcohol, does not seem to be identical with erythrene bromide, since the former decomposes without volatilising, whilst the latter distils completely although with partial decomposition.

Erythrene from coal-gas combines with hypochlorous acid, forming a compound which is soluble in ether, alcohol, or water.

C. H. B.

Triethyl Carbinol. By S. Barataeff and A. Saytzeff (*J. pr. Chem.* [2], **34**, 463—467).—Triethyl carbinol is obtained by bringing together diethyl ketone (1 mol.), ethylic iodide (3 mols.), and excess of zinc. At the end of a week, the mass is treated with water, the zinc oxide dissolved in sulphuric acid, and the liquid distilled. A colourless liquid of camphor-like odour boiling at 141—143° (uncorr.) is obtained. Sp. gr. at 20° = 0·84016 (water at 20° = 1). The acetate is an oil boiling at 160—163°.

Triethyl carbinol when oxidised with chromic mixture gives diethyl ketone, heptylene, propionic and acetic acids, and carbonic anhydride. The triethyl carbinol obtained as above is identical with that obtained by Nachapetian from zinc ethyl and propionic chloride (this Journal, 1871, 1035). H. K. T.

Dipropyl Carbinol. By D. Ustinoff and A. Saytzeff (*J. pr. Chem.* [2], **34**, 468—472).—Butyrone, propyl iodide, and zinc are allowed to react as in the previous paper. On treating with water and distilling, *dipropyl carbinol* is obtained as a colourless liquid boiling at 154—155°. Sp. gr. at 20° = 0·82003 (water at 20° = 1). The acetate boils at 170—172°. With chromic mixture, the dipropyl carbinol is oxidised first to butyrone, and then to propionic and butyric acids. H. K. T.

Action of Silver Acetate on Tetrabromodiallyl Carbinol Acetate. By W. Dieff (*J. pr. Chem.* [2], **35**, 17—21).—Saytzeff obtained (*Annalen*, **185**, 138), by the action of silver acetate on the compound $OH{\cdot}CAc(CH_2{\cdot}CHBr{\cdot}CH_2Br)_2$, a product which he took to be the acetate of an alcohol of the formula

$$OH{\cdot}CH[CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH]_2.$$

The author repeated the experiment, and determined the number of acetyl-groups by heating the compound with alcoholic potash. The numbers obtained corresponded with the formula of a triacetyl-compound, $C_7H_{11}O(OAc)_3$. This compound was also prepared by heating the alcohol (obtained by saponifying the acetate) with an excess of acetic anhydride at 145° for 12 hours. The sp. gr. of the triacetyl-compound at 0° = 1·18013 (water at 0° = 1). When saponified by means of baryta, it yields the compound $C_7H_{11}O(OH)_3$. The latter is a viscous syrup, readily soluble in water and alcohol. It is identical with the compound which Saytzeff (*loc. cit.*) obtained by saponifying the ether with alcoholic solution of hydrogen chloride.

N. H. M.

Erythrol. By A. Colson (*Compt. rend.*, **104**, 113—115).—The heat of solution of erythrol at 18° is −5·2 cal., and at 9° −5·12 cal.

The heat of neutralisation is affected by the degree of dilution of the solution. The value obtained for the first equivalent of potash was +0·66 cal., and for the second equivalent +0·44 cal. The thermochemical results are not in accord with the generally accepted symmetrical constitution of erythrol.

When erythrol is treated with phosphoric bromide, it yields a bromhydrin, $C_4H_6Br_4$, which melts at 112°, dissolves in 10 parts of boiling ether, and is identical with the crotonylene tetrabromide described by Henninger. If heated with bromine in sealed tubes at 175°, it yields a mixture of a solid and a liquid product. The solid has the composition $C_4H_4Br_6$, and crystallises in nacreous plates which melt at 167—169°, and dissolve readily in chloroform, but are only slightly soluble in alcohol or ether; sp. gr. about 3·4.

The liquid compound is an isomeride of the solid product. It dissolves easily in chloroform or ether, but is only slightly soluble in alcohol; sp. gr. about 2·9 at 15°. When heated with dilute potash in sealed tubes at 120—130° for several hours, it yields a potassium salt which resembles potassium hydrogen tartrate in appearance, but the angles of the crystals are different, and the crystals have no action on polarised light. Its solutions give no precipitate with salts of calcium or silver, but a precipitate is formed with salts of lead. This compound is in all probability the potassium salt of erythric acid, and this supposition is confirmed by the weight of lead salt obtained from a given weight of the potassium salt.

It would seem, therefore, that the liquid is the unsymmetrical $CBr_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, whilst the solid is the symmetrical

$$CHBr_2{\cdot}CHBr{\cdot}CHBr{\cdot}CHBr_2.$$

This result requires confirmation, but it is evident that the complete hydrolysis of the bromine-derivatives of crotonylene is possible, since the acid obtained was free from bromine. C. H. B.

Glucose and the Saccharification of Starch. By L. Cuisinier (*Chem. Centr.*, 1886, 614).—The sugar found in the soluble part of barley- or maize-meal consists for the most part of dextrose. If this dextrose is formed by the action of diastase, then the ferment must exert a different action on raw starch from what it does on boiled starch. The dextrose may, on the other hand, be formed by another special ferment present in the living grain. This latter view of the case is, according to the author's experiments, the correct one. The ferment present in ungerminated grain converts starch slowly into dextrose. The dextrose so formed is readily crystallisable on concentrating the liquid, the crystals obtained consisting almost exclusively of fermentable sugar contaminated with not more than 1 to 2 per cent. of dextrin. J. P. L.

Action of Saliva on Starch. By E. Bourquelot (*Compt. rend.*, **104**, 71—74).—Potato-starch, free from glucose, was heated with water to a definite temperature, cooled down to the ordinary temperature, and then mixed with saliva. When fermentation was complete, the reducing power of the liquid was determined by means of Fehling's

solution. The saliva acts only on the starch which has undergone hydration, and it was found that the hydrating action of water begins at about 53°, and increases somewhat irregularly up to 74°, beyond which point an increased temperature exerts no sensible effect.

In a second series of experiments, the water and saliva were mixed together, heated up to a definite temperature, the starch added, the temperature maintained for about $3\frac{1}{2}$ hours, and the reducing power of the liquid was then determined. The results show that saliva acts on starch at a temperature below that at which water alone exerts any hydrating action. Feebly acid or alkaline liquids, or solutions of sodium chloride or phosphate have no action on amylose at temperatures below 53°, and saliva in which the ferment has been destroyed by boiling is scarcely more active. It follows that it is the diastase in the saliva which assists the hydrating action of the water.

At the temperature at which water alone begins to convert starch into a hydrate saccharifiable by saliva at the ordinary temperature, water mixed with saliva has a more energetic action than when water and saliva are allowed to act successively in the way described. The difference diminishes, however, as the temperature approaches 58°, at which point the two actions are equal. At higher temperatures, the action is greater if the water alone is heated, and the saliva is afterwards added to the cooled liquid, than when the saliva and water are heated together, since the high temperature destroys the diastase in the saliva. C. H. B.

Starch Granules. By E. Bourquelot (*Compt. rend.*, **104**, 177—180).—Potato-starch was heated with saliva and water at different temperatures for different periods of time. At temperatures below 57°, the amount of reduction increases with the temperature and also with the time, but is not proportional to the latter. At temperatures above 57°, however, the action continues to increase with the temperature, but attains its maximum in about five hours, and proceeds very little further even if the experiment is prolonged to 30 hours.

The hydrating action of water alone increases with the temperature, and is practically complete after five hours, increasing but little if the experiment is continued for 30 hours. The hydrating action of the water is independent of the mass of the water.

It is a general rule that a reaction effected on a single carbon compound is proportional to, or in direct relation to, the time, especially if the action is of the nature of hydration. The divergence from this rule observed in the case of starch and water indicates that starch granules are composed of a complex mixture of carbohydrates, and not only of one or two compounds (granulose and amylose). Possibly these different compounds are polymerides of one original substance. This view is similar to that held by many physiologists concerning the different layers of cellulose which constitute cell-walls. C. H. B.

Inosite. By Maquenne (*Compt. rend.*, **104**, 225—227).—Walnut leaves are extracted methodically with about four times their weight of water, and the boiling solution is precipitated first with milk of

lime, then with lead acetate, and finally with basic lead acetate, which forms an insoluble compound with the inosite. The last precipitate is washed with water, decomposed by hydrogen sulphide, and the solution concentrated to a syrup. The boiling liquid is then mixed with 7 or 8 per cent. of concentrated nitric acid, which destroys nearly all the foreign matter without attacking the inosite, and, after cooling, a mixture of 4—5 vols. of alcohol with 1 vol. of ether is gradually added to the nearly colourless liquid. Inosite is thus separated as a colourless flocculent precipitate, which is recrystallised from dilute acetic acid, dissolved in water, again treated with nitric acid, and again precipitated with alcohol and ether. A small quantity of calcium sulphate, which always occurs in the product, is decomposed by adding barium hydroxide, and the barium is removed by means of ammonium carbonate, the product being finally recrystallised from water. The yield is about 2·94 grams per kilo. of leaves.

Anhydrous inosite has the composition $C_6H_{12}O_6$, whilst the crystals have the composition $C_6H_{12}O_6 + 2H_2O$; they lose all their water at 110°. Inosite does not volatilise without decomposition, but its molecular weight can be determined by Raoult's cryoscopic method, that is, by determining the freezing point of its aqueous solution. The freezing point of a solution of 2·5 grams of inosite in 100 grams of water is −0·29°, whilst the calculated value for $C_6H_{12}O_6$ is −0·27°.

Inosite is only slightly soluble in cold, but very soluble in warm water. It is insoluble in alcohol, ether, and glacial acetic acid, but dissolves readily in dilute acetic acid, from which it can be easily crystallised. It melts at 217° without carbonisation, and boils with slight decomposition in a vacuum at 319°. When heated in the air, it burns readily. Solutions of inosite are optically inactive, both when freshly prepared and after they have been in contact with *Penicillium glaucum* for six weeks. Inosite is not attacked by boiling dilute acids or alkalis, does not reduce copper solutions, and is not acted on by ammoniacal silver nitrate alone, but in presence of sodium hydroxide it yields a mirror of metallic silver. It does not combine with sodium hydrogen sulphite, is not reduced by sodium amalgam, and is not sensibly affected by halogens in the cold. When heated with bromine and water at 100°, it yields brown products precipitable by salts of barium and similar to those obtained in Scherer's reaction. These compounds contain no bromine, and are oxidation-products which can be more readily prepared by the action of nitric acid.

No acid containing six carbon-atoms can be obtained from inosite, nor will it split up into oxy-acids of the acetic series. It is neither an aldehyde nor a ketone, and contains neither double bonds nor lateral chains; hence, it can only be a hexhydric hexa-secondary alcohol, with a constitution represented by the symbol—

$$\overset{\cdot}{O}H\cdot CH<\begin{matrix}CH(OH)\cdot CH(OH)\\ CH(OH)\cdot CH(OH)\end{matrix}>CH\cdot OH,$$

which agrees with its optical inactivity. C. H. B.

Preparation of Isobutylamines. By H. Malbot (*Compt. rend.*, **104**, 63—65).—When isobutyl chloride is heated with an equivalent

quantity of ammonia dissolved in water or isobutyl alcohol, it yields the three isobutylamines, the tri-isobutylamine being formed in largest proportion. If aqueous ammonia is used, the composition of the product is monisobutylamine, 1 part; di-isobutylamine, 4 parts; tri-isobutylamine, 5 parts. This result differs from that obtained by Reimer (*Ber.*, **3**, 756) by acting on isobutyl bromide with ammonia dissolved in ordinary alcohol. C. H. B.

Separation of Mono- and Di-isobutylamines by Means of Ethyl Oxalate. By H. Malbot (*Compt. rend.*, **104**, 228—231; see preceding Abstract).—In the first fraction, which is rich in monisobutylamine, it is necessary to produce the maximum quantity of di-isobutyloxamide without neglecting to collect the two oxamates which are also formed. In the second fraction, rich in di-isobutylamine, the bases are converted into oxamates, which are then separated by a method more perfect than distillation.

The operations by which these changes are effected are: (1) Ethyl oxalate is added to the *aqueous* solution of the bases, and the primary bases are thus converted into oxamides; (2), the mixture of anhydrous bases, poor in primary bases, is poured into ethyl oxalate, and primary and secondary bases are thus converted into oxamates; (3), the tertiary bases are separated by distillation, and the oxamates are saponified by calcium hydroxide at a moderate temperature, the calcium oxamates being separated by crystallisation.

Di-isobutyloxamide forms short, acute lamellæ, which are almost insoluble in boiling water, but crystallise from boiling alcohol in long, brilliant, slender needles which melt at 167°, and sublime slowly at this temperature without decomposition.

Calcium isobutyloxamate is obtained by heating the anhydrous isobutylamine with ethyl oxalate, and then treating the product, which boils at 160°, with calcium hydroxide. It crystallises from alcohol in anhydrous needles.

Calcium di-isobutyloxamate, formed in a similar manner, is separated from the preceding compound by fractional crystallisation, since it is more soluble in alcohol, from which it crystallises in slender, flexible, silky needles. C. H. B.

Syntheses of Guanylcarbamide. By E. Bamberger (*Ber.*, **20**, 68—71).—Guanylcarbamide can be obtained by methods similar to those employed in the synthesis of carbamide, guanidine being substituted for ammonia. Thus, the base is formed when an intimate mixture of guanidine carbonate (1 part) and urethane (2 parts) is heated at 160° until alcohol ceases to distil over, $NH_2{\cdot}COOEt + (NH_2)_2C{:}NH = NH_2{\cdot}CO{\cdot}NH{\cdot}C(NH)NH_2 + EtOH$. At the same time, sparingly soluble decomposition products of guanidine, showing properties similar to those of ammeline, ammelide, and melanurenic acid, are formed, with evolution of ammonia; the guanylcarbamide can be separated from these by extracting the melt with water, and converting the base into the copper-derivative. Another synthesis, which for its success depends on the observance of several minute precautions, can be effected by heating at about 180° an intimate mixture of potassium

cyanate and guanidine hydrochloride. From an aqueous solution of molecular proportions of these salts and of hydrochloric acid in the cold, guanylcarbamide cannot be separated, although it seems to be formed since the solution gives the copper reaction of the base.

Guanylcarbamide nitrate, $C_2N_4H_6O,HNO_3$, crystallises in white needles, the *aurochloride* in sparingly soluble, long, golden-yellow needles.

Guanidine cyanurate, $CN_3H_5,(CNOH)_3$, obtained by adding guanidine carbonate to a boiling solution of cyanuric acid, crystallises in silky needles. W. P. W.

Preparation of Alkylamidoformic Chlorides and Alkyl Isocyanates. By L. Gattermann and G. Schmidt (*Ber.*, **20**, 118—121).—When a stream of phosgene gas is passed over dry ethylamine hydrochloride heated at 250—270°, *ethamidoformic chloride*,

NHEt·COCl,

is formed in almost theoretical quantity. It is a colourless liquid, boiling at 92°, and having a very pungent odour. During the distillation, there is a dissociation into hydrogen chloride and ethyl isocyanate, but on cooling the chloride is re-formed. This compound is decomposed by water into ethylamine hydrochloride and carbonic anhydride. This substance is identical with that obtained by Habich and Limpricht by the action of hydrochloric acid on ethyl isocyanate, and by the distillation of diethylcarbamide hydrochloride. When the above chloride is distilled over quicklime, ethyl isocyanate is formed in almost the theoretical proportion.

This chloride, when treated with toluene and aluminic chloride, yields *paratoluylethamide*, $C_6H_4Me·CO·NHEt$, which crystallises in colourless, glistening needles, melting at 96°; this, when heated with strong potash, yields paratoluic acid. When benzene is substituted for toluene in the above reaction, *ethylbenzamide*, Ph·CO·NHEt, is formed, which forms glistening needles, melting at 67°, and boiling at 258—260°.

Methylamine hydrochloride and phosgene gas yield *methamidoformic chloride*, NHMe·COCl. This crystallises in scales, melts at 90°, and boils (with dissociation) at 93—94°. In its properties and reactions, it resembles the ethyl-derivative. With toluene and aluminic chloride, it gives *paratoluylmethamide*, $C_6H_4Me·CO·NHMe$. This is soluble in water, crystallises in colourless plates, and melts at 143°.

The above reactions appear to be generally applicable for the preparation of substituted amidoformic chlorides and of alkyl isocyanates. L. T. T.

Convenient Method for Preparing Brominated Fatty Acids. By A. Michael (*J. pr. Chem.* [2], 92—95).—The chlorides of monobasic fatty acids are heated in a flask with the calculated amount of carefully dried bromine and about 50 c.c. of carbon bisulphide, until no more hydrogen bromide is evolved. The product is poured into water, partially distilled, and converted into the ethereal salt by treatment with absolute alcohol. From butyric acid, nearly the theoretical amount of ethyl α-bromobutyrate was obtained. The method works

well in the case of monobasic fatty acids, but not so well with succinic chloride, owing to the instability of the bromine-derivative when warmed. N. H. M.

Behaviour of Acetic Acid and some of its Derivatives towards Phosphorus Pentachloride. By A. Michael (*J. pr. Chem.* [2], **35**, 95—96).—When acetic chloride (40 grams) is boiled with phosphorus pentachloride (200 grams) for some weeks, mono- and tri-chloracetic acids are formed (probably also some dichloracetic acid). Much acetic and phosphoric chlorides remained unchanged.

When chloracetic acid and phosphorus pentachloride (1 mol. to 4 mols.) are heated for two days, perchlorethylene is formed, together with higher boiling substances, probably tetra- and penta-chlorethane.

Phosphorus pentachloride and phenoxyacetic acid react violently when brought together in the cold. The product consists of trichlorophenoxyethylene (Abstr., 1886, 614) and a substance crystallising in rhombic prisms melting at 151—152°. The latter has the composition of a chlorophenoxyacetic acid. N. H. M.

β-Dimethacrylic Acid. By D. Ustinoff (*J. pr. Chem.* [2], **34**, 478—485).—The salts of β-dimethacrylic acid (Semljanitzin and Saytzeff, Abstr., 1879, 618) are described. The sodium salt, $C_5H_7O_2Na$, forms white, opaque, effloresced crystals. The calcium salt, $(C_5H_7O_2)_2Ca$, forms bundles of long, silky crystals belonging to the rhombic system, soluble in water and alcohol. The barium salt, $(C_5H_7O_2)_2Ba + 2H_2O$, nodular groups of prismatic crystals. The zinc salt,

$$(C_5H_7O_2)_2Zn + 4H_2O,$$

crystallises in rhombic plates. The copper salt, $(C_5H_7O_2)_2Cu + 2H_2O$, crystallises in efflorescent rhombic plates. The lead salt, $(C_5H_7O_2)_2Pb + H_2O$, forms bundles of needles, and the silver salt, $C_5H_7O_2Ag$, is a crystalline powder. When β-dimethylacrylic acid is treated in ethereal solution with bromine, it forms a dibromide, $C_5H_8Br_2O_2$; this is a crystalline substance melting at 105—106°. The salts and bromine compound of β-dimethyacrylic acid distinguish it from its isomerides, angelic, methylcrotonic, and allylacetic acids.

H. K. T.

Acids from Drying Oil. By K. Hazura (*Monatsh. Chem.*, **7**, 637—638).—When linoleic acid is oxidised with potassium permanganate in alkaline solution, *linusic acid*, $C_{18}H_{36}O_7$, is formed. It crystallises in lustrous needles, very sparingly soluble in water, and melts at 188°.

The acid contained in hemp-oil yielded a *tetrabromo-derivative* melting at 114—115°, and a hexabromo-derivative melting at 177°; the latter compound is amorphous. The analyses of the two compounds make it probable that the formula of the original acid is $C_{18}H_{32}O_2$, and not $C_{16}H_{28}O_2$. N. H. M.

Methoxydiallylacetic Acid and its Salts. By S. Barataeff (*J. pr. Chem.* [2], **35**, 1—6).—Methoxydiallylacetic acid (Abstr., 1885, 512) is readily soluble in alcohol, ether, and hot water. The

ethyl salt boils at 214—216°. Sp. gr. = 0·96228 at 28° (water at 20° = 1). Determinations of the refractive power of the ethyl salt point, according to Brühl's law, to the presence of two double affinities; this was confirmed by the formation of a *bromine-derivative*, $C_{11}H_{18}O_3Br_4$, by the action of bromine on the salt. *Barium methoxydiallylacetate* crystallises with 2 mols. H_2O in needles, rather readily soluble in water; the *calcium salt* forms slender crystals, more sparingly soluble than the barium salt; the *zinc salt* crystallises in microscopic, slender needles, very soluble in water; the *lead salt* (with $6\frac{1}{2}$ mols. H_2O) separates from its solution when slowly evaporated at 10°, in large, triclinic prisms, rather sparingly soluble in water, and more soluble in alcohol. The *copper salt*, with 1 mol. H_2O, separates from the warm aqueous solution in bright green, oily drops, which solidify on cooling; the *silver salt* separates in thin threads, rather soluble in water.

N. H. M.

Oxalic Acid from the Residue of Spiritus Ætheris Nitrosi. By H. Frickhinger (*Arch. Pharm.* [3], **24**, 1065—1068).—By taking alcohol of 0·812 sp. gr. instead of 0·832, as given in the German Pharmacopœia, almost the whole of the liquid may be distilled over, and there is much less free acid to contend with in the distillate. The nitric acid is not sufficient in amount to completely oxidise all the products of the reaction. The residue from the first distillation, amounting to about 2 per cent. of the original charge, is wine-yellow, strongly acid, and has a specific gravity of 1·10. It contains no nitric acid, but, on the contrary, a large quantity of oxalic acid, which can be economically converted into ammonium oxalate. If this residue is poured into nitric acid of 1·35 sp. gr., and allowed to stand for some weeks, crystals of oxalic acid separate out from the grass-green liquid obtained. The mother-liquor becomes again colourless on warming for some time. The rectified ether is perfectly neutral in reaction; at first the sp. gr. of the distillate is 0·835, then 0·840, 0·845, and 0·850, at which point it remains until the rectification suddenly ceases.

J. T.

Preparation of Ethyl Oxalate. By E. Schatzky (*J. pr. Chem.* [2], **34**, 500—501).—A better yield of the oxalate is obtained by maintaining the mixture of oxalic acid and alcohol in ebullition for some hours, then distilling off any ethyl formate formed, adding more alcohol, and again boiling. By this means 56·03 per cent. of the theoretical yield is obtained.

H. K. T.

Action of Ethyl Iodide and Zinc on Ethyl Malonate. By C. Daimler (*Ber.*, **20**, 203—204).—When a mixture of ethyl malonate (1 mol.) and ethyl iodide (2 mols.) is heated with zinc, ethane is evolved, and ethylic ethylmalonate is obtained; the yield amounts to 90 per cent. of that required by theory. The author finds that ethylmalonic acid yields two barium salts, one $(C_5H_7O_4)_2Ba + H_2O$, which crystallises in hemispherical aggregates, and is converted into barium butyrate at 100°, and a second, $C_5H_6O_4Ba + \frac{1}{2}H_2O$, which forms slender, lustrous prisms, very sparingly soluble in water. When, in the above reaction, 4 mols. instead of 2 mols. of ethyl iodide are

employed, an almost quantitative yield of ethyl diethylmalonate is obtained. W. P. W.

Action of a Mixture of Allyl and Ethyl Iodides and Zinc on Ethyl Oxalate. By S. Barataeff (*J. pr. Chem.* [2], **35**, 7—16).—A mixture of ethyl oxalate (1 mol.), allyl iodide (1 mol.), and ethyl iodide (2 mols.) was added by drops to finely granulated zinc in a retort kept cold by means of ice. The contents of the retort were left for 24 hours, and then heated in a water-bath for 10 hours. The product was then treated with sulphuric acid to dissolve the zinc oxide, and distilled. The oil so obtained was fractionally distilled, and was found to consist of a mixture of ethylic diethyloxalate and diallyloxalate. The reaction is analogous to that which takes place between allyl and ethyl iodide, zinc and ethyl formate (Kanounikoff and Saytzeff, this Journal, 1877, ii, 298). N. H. M.

Diallyloxalic Acid. By E. Schatzky (*J. pr. Chem.* [2], **34**, 485—500).—The following data were obtained for the optical relations of diallyloxalic acid:—

For a 7·08 per cent. solution in benzene at 18·6°—

$$D^{t} = 0{\cdot}88981,\ n_a = 1{\cdot}494830,\ n_\beta = 1{\cdot}151107,\ A = 1{\cdot}475135.$$

$$B = 0{\cdot}849372,\ \frac{n_a - 1}{D} = 0{\cdot}55611,\ \frac{A - 1}{D} = 0{\cdot}53397.$$

For the acid—

$$\frac{n_a - 1}{D} = 0{\cdot}4487,\ P\frac{n_a - 1}{D} = 69{\cdot}99,\ R_a = 64{\cdot}6.\ \text{Difference } 5{\cdot}39.$$

$$\frac{A - 1}{D}\ 0{\cdot}42991,\ P\frac{A - 1}{D} = 67{\cdot}07,\ R_A = 63{\cdot}07.\ \text{Difference } 4{\cdot}00.$$

The ammonium, sodium, potassium, lithium, silver, calcium, barium, magnesium, lead, copper, cadmium, and zinc salts have been prepared.

Ethyl diallyloxalate combines with bromine, forming a yellowish-brown liquid of the formula $C_{10}H_{16}Br_4O_3$.

Diallyloxalic acid when treated with bromine gave a neutral substance, crystallising in microscopic needles, insoluble in water, soluble in alcohol, ether, and benzene, and melting at 42—43°. The substance is scarcely acted on by sodium carbonate; with potassium hydroxide no definite results were obtained. It is probably a tribromolactone formed from the tetrabromodiallyloxalic acid by removal of hydrogen bromide. Diallyloxalic acid combines with hydrogen chloride, forming a thick liquid, $OH{\cdot}C(C_3H_6Cl)_2{\cdot}COOH$.

Diallyloxalic acid is converted by concentrated hydriodic acid into iododiallylacetic acid, from which diallylacetic acid can be obtained by means of sodium amalgam, hence diallyloxalic acid has the formula $OH{\cdot}C(C_3H_5)_2{\cdot}COOH$. H. K. T.

Action of Ethyl Chloracetate and Zinc on Ethyl Oxalate. By R. Fittig and C. Daimler (*Ber.*, **20**, 202—203).—When a mixture of ethyl oxalate (1 mol.) and ethyl chloracetate (2 mols.) is heated with

zinc at 100° for several days, a dark-brown zinc compound is obtained, which is readily decomposed by water with formation of a bright yellow, amorphous substance, but when treated with dilute sulphuric acid, and extracted with ether, yields a thick oil, probably identical with Wislicenus' ethyl oxalacetate (this vol., p. 234), and a colourless, well crystallised compound, *ethyl ketipate* (ketone-adipate), $C_{10}H_{14}O_6$. This is a salt of a bibasic ketonic acid, whose constitution is probably either $COOEt\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot COOEt$ or $COOEt\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOEt$. It melts at 76—77°, is decomposed by boiling water, and is readily soluble in ether, chloroform, alcohol, benzene, and carbon bisulphide. Ferric chloride colours the alcoholic solution an intense red. With phenylhydrazine, a compound, $C_4H_4(N_2C_6H_6)_2(COOEt)_2$, is obtained, crystallising from chloroform in yellow needles. Aqueous barium and calcium hydroxides precipitate white insoluble compounds of the formula $C_{10}H_{12}O_6Ba$(or Ca) + H_2O. By the action of bromine, according to the conditions of the experiment, there is obtained either a tetrabromo-substitution-derivative, $C_4O_2Br_4(COOEt)_2$, crystallising in yellow prisms, or a partially saponified compound of the formula $C_4O_2H_2Br_2(COOH)COOEt$, forming colourless crystals.

Ketipic acid is a white powder, insoluble in ordinary solvents, and is very unstable. When heated, it decomposes into carbonic anhydride and a yellow liquid, which boils at 78—79°, and has an odour resembling that of quinone. W. P. W.

Nitration of α-Thiophenic Acid. By M. Römer (*Ber.*, **20**, 116—118).—When α-thiophenic acid is gradually added to concentrated nitric acid at 50°, *nitro-α-thiophenic acid*, $NO_2\cdot C_4SH_2\cdot COOH$, is formed. This acid exists in two modifications, the one crystallising in long, thin, colourless needles melting at 145—146°, the other in compact crystals melting at 125°. From an aqueous solution, the needles crystallise out first, and afterwards the compact variety. By recrystallisation, the latter modification is always partially, sometimes wholly, converted into the needles, whilst when placed under water, the needles are gradually changed into the compact variety. This behaviour resembles that of dinitrothiophen. With a trace of soda, both modifications of the acid give a magenta-red coloration which is destroyed by excess of alkali. The *silver salt* forms colourless needles; the *ethyl salt* colourless needles, melting at 70—71°, and subliming unchanged; the *copper salt* forms bluish-green hydrated prisms.

L. T. T.

Constitution of Benzene. By A. Baeyer (*Ber.*, **19**, 1797—1810; see also this vol., p. 370), by J. Thomsen (*Ber.*, **19**, 2944—2950), and by A. Ladenburg (*Ber.*, **20**, 62—65).—Theoretical papers: an account of the arguments brought forward will be found in the present number of the Transactions (A. K. Miller, Trans., 1887, 208—215).

Chlorination of Toluene. By E. Seelig (*Annalen*, **237**, 129—181).—The trichlorotoluenes have already been described by the author (Abstr., 1885, 769). Pure orthochlorotoluene can be obtained

by taking advantage of the facts that orthochlorotoluene is more easily converted into the sulphonic acid than the para-compound, and also that calcium and sodium orthochlorotoluene-sulphonates are less soluble than the corresponding para-salts. The sulphonic acid when decomposed by superheated steam, yields orthochlorotoluene. The pure compound boils at 156° under 750 mm. pressure. The chief product of the chlorination of orthochlorotoluene is *α*-dichlorotoluene, $C_6H_3MeCl_2$ [1 : 2 : 3]. Parachlorotoluene is completely converted into *β*-dichlorotoluene [Me : Cl_2 = 1 : 2 : 4].

α-Dichlorotoluene boils at 195—199° and *β-dichlorotoluene* boils at 194—198°. The former yields a dinitro-derivative melting at 121—122°. *β*-Dinitrodichlorotoluene crystallises in prisms, and melts at 101—102°. The *α*-diamine crystallises in needles and melts at 137°; the *β*-diamine melts at 110°, and is deposited from light petroleum in long needles.

β-Dichlorobenzyl chloride and aldehyde are obtained from *β*-dichlorotoluene. The aldehyde melts at 71°, and boils between 231° and 235°. On oxidation, it yields dichlorobenzoic acid [1 : 3 : 4]. *β*-Dichlorocinnamic acid is deposited from weak alcohol in needles, and melts at 228°. W. C. W.

Nitrochlorotoluene and Chlorotoluidine. By H. Goldschmidt and M. Hönig (*Ber.*, **20**, 199—201).—*Nitrochlorotoluene*,

$$C_6H_3MeCl{\cdot}NO_2\ [= 1 : 2 : 5],$$

obtained by diazotising nitrotoluidine, $C_6H_3Me(NH_2){\cdot}NO_2$ [= 1 : 2 : 5], crystallises in needles, melts at 44°, boils without decomposition at 248° under 711 mm. pressure, and is readily soluble in ether.

Chlorotoluidine, $C_6H_3MeCl{\cdot}NH_2$ [Me : Cl : NH_2 = 1 : 2 : 5], is formed when the nitro-compound is reduced with tin and hydrochloric acid. It melts at 83°, boils at 239° under 715 mm. pressure, and is identical with Wroblewsky's chlorotoluidine and that obtained when orthochlorotoluene is nitrated and reduced (Abstr., 1886, 1022). The *hydrochloride* crystallises in long, slender needles; the *acetyl*-derivative crystallises from benzene in colourless scales melting at 89°; and the *phenylthiocarbamide* forms small, white granules melting at 108—109°. W. P. W.

Synthesis of Cyanphenine. By P. Klason (*J. pr. Chem.* [2], **35**, 82—84). **Remarks.** By E. v. Meyer (*ibid.*, 84—85).—By the action of potassium on ethyl cyanide, Kolbe and Frankland (*Annalen*, **65**, 281) obtained ethane together with cyanethine. In a similar manner Hofmann obtained cyanphenine from benzonitrile, and Bayer cyanmethine from acetonitrile (*Ber.*, **1**, 198, and **2**, 319). It is, therefore, probable that these compounds have an analogous constitution.

Cyanphenine is obtained by dissolving pure cyanuric chloride in pure ether, and adding the calculated amount of bromobenzene and sodium. It is filtered, the ether distilled off, and the residue treated with water and crystallised, first from glacial acetic acid and then from alcohol. The chief product of the reaction is *diphenyl-*

cyanine chloride, $(CN)_3ClPh_2$; this is more soluble than cyanphenine, and crystallises in groups of needles melting at 136°. The formation of cyanphenine in the above reaction shows it to be a triphenyl-cyanuric compound.

v. Meyer refutes Klason's view that cyanethine and cyanmethine are cyanuric compounds. Cyanmethine and cyanethine are both converted by the action of nitrous and hydrochloric acids into hydroxy-bases, the hydroxyl taking the place of amidogen. Ethyl and methyl cyanides contain hydrogen-atoms more loosely combined than in phenyl cyanide; hence it is conceivable that in polymerising, hydrogen-atoms disunite in the case of the fatty cyanides, whilst phenyl cyanide polymerises without shifting of hydrogen to cyanur-phenyl, $(CN)_3Ph_3$. N. H. M.

Quinol and its Derivatives. By A. Baessler (*Chem. Centr.*, 1886, 671—672).—*Amidodimethylquinol*, $C_6H_3(OMe)_2{\cdot}NH_2$, is prepared by reducing mononitrodimethylquinol in acetic acid solution with sodium amalgam. It melts at 81—82°. The chloride crystallises in white needles, which deliquesce in the air; the platinochloride forms a brown precipitate. From the aqueous solution of the base, iron chloride on warming throws down greenish plates with a strong metallic lustre, which dissolve in water with a red colour. From the hydrochloric acid solution, potash precipitates the substance in black flocks; solutions of silver salts are reduced, giving a mirror. *Acetamidodimethylquinol*, $C_6H_3(OMe)_2{\cdot}NHAc$, is formed by dissolving the base in acetic anhydride. It crystallises in brilliant scales, and melts at 91°. *Nitracetamidodimethylquinol*, $NO_2{\cdot}C_6H_2(OMe)_2{\cdot}NHAc$, is prepared by slowly adding the preceding compound to fuming nitric acid. It melts at 164°.

Dimethylquinoltrimethylammonium iodide, $C_6H_3(OMe)_2{\cdot}NMe_3I$, is obtained by heating the substance with methyl iodide and methyl alcohol in sealed tubes at 150°. It melts at 202°. The chloride melts at 172°; the platinochloride is a beautiful, yellow, crystalline precipitate.

Dimethylquinolphenylthiocarbamide, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_6H_3(OMe)_2$, formed by adding phenylthiocarbamide in excess to an alcoholic solution of amidodimethylquinol, melts at 137°. The *thiocarbamide-derivative* of amidodimethylquinol, $CS[NH{\cdot}C_6H_3(OMe)_2]_2$, melts at 109°.

Azodimethylquinol, $[C_6H_3(OMe)_2]_2N_2$, is formed when nitrodimethylquinol is reduced by sodium amalgam in alkaline solution, or by the action of alcoholic potash and zinc-dust on the mononitro-compound. It forms red needles, and melts at 140°. It dissolves in strong hydrochloric acid with a dark blue colour, in strong sulphuric acid with a violet colour, which afterwards changes to blue and green, with partial decomposition; with alcoholic bromine solution, it forms *dibromazodimethylquinol*, which melts at 220°.

Hydrazodimethylquinol, $C_6H_3(OMe)_2{\cdot}NH{\cdot}NH{\cdot}C_6H_3(OMe)_2$, is obtained together with the preceding substance by the reaction given above.

Tetramethoxydiamidodiphenyl, $NH_2{\cdot}C_6H_2(OMe)_2{\cdot}C_6H_2(OMe)_2{\cdot}NH_2$, is

obtained when the mixture of the azo-compound and the preceding substance is treated with warm hydrochloric acid. It melts at 210°. The chloride is easily soluble in water: the platinochloride quickly becomes brown in the air. With phenylthiocarbamide, it forms a compound, $C_{12}H_4(OMe)_4(NH{\cdot}CS{\cdot}NHPh)_2$, which melts at 184°; acetic anhydride gives the *diaceto-compound*, $C_{12}H_4(OMe)_4(NHAc)_2$, which melts at 251°, and gives golden-yellow plates when treated with nitric acid. The corresponding benzoyl-derivative is obtained by boiling tetramethyoxydiamidodiphenyl with benzoic chloride; it melts at 305°. G. H. M.

Isomeric Mono- and Di-benzoylphenylhydrazines. By A. Michaelis and F. Schmidt (*Ber.*, **20**, 43—48).—Sodium phenylhydrazine is suspended in benzene, the mixture well cooled with ice-water, and benzoic chloride diluted with benzene gradually added, the vessel being from time to time removed from the ice-water to prevent solidification of the benzene. When the reaction is completed and the contents of the vessel no longer smell of benzoic chloride, the benzene is distilled off, and the nearly colourless residue repeatedly extracted with ether, which dissolves the new unsymmetrical monobenzoylphenylhydrazine, and leaves a residue consisting of the sparingly soluble symmetrical mono- and di-benzoylphenylhydrazines. The ethereal extract, after distilling off the ether, yields a viscous red oil, which is poured into water, excess of concentrated hydrochloric acid added, and the separated hydrochloride washed with and repeatedly crystallised from water containing hydrochloric acid.

Unsymmetrical benzoylphenylhydrazine, $NH_2{\cdot}NPhBz$, obtained by decomposing the hydrochloride with sodium carbonate, crystallises in thin, colourless needles, melts at 70°, and is very readily soluble in ether, alcohol, and chloroform, and sparingly in cold water. It is a feeble base, does not reduce Fehling's solution in the cold, but does so readily on heating, does not reduce ammoniacal silver solution even when heated, and is without action on yellow mercuric oxide. When heated with concentrated hydrochloric acid at 150°, it is decomposed into benzoic acid and phenylhydrazine. The *hydrochloride*, $NH_2{\cdot}NPhBz,HCl$, forms colourless needles, melts at 202°, and is soon decomposed by water. When an aqueous solution of the hydrochloride is treated with aqueous soda, a sodium-derivative, $C_{13}H_{11}NaN_2O$, separates as a thick, white precipitate. The formation of this compound is peculiar, and suggests a doubt as to whether an amido-group is present in the base, or if it should not rather be represented by the formula $<^{NH-}_{NPh}>CPh{\cdot}OH$.

The *dibenzoylphenylhydrazine* obtained in this reaction has the same melting point (178°) as that obtained by Fischer (Abstr., 1878, 309), but differs from it in not reducing ammoniacal silver nitrate. It is also obtained by the action of benzoic chloride on the unsymmetrical benzoylphenylhydrazine. It probably should be represented by the formula $<^{NBz}_{NPh}>CPh{\cdot}OH$, Fischer's compound being the true dibenzoyl-derivative, $NPhBz{\cdot}NHBz$.

Diacetylphenylhydrazine, N_2HPhAc_2, is obtained by the action of acetic chloride on sodium or potassium phenylhydrazine; it crystallises in nodular groups of needles, melts at 106°, is readily soluble in water, alcohol, and chloroform, very sparingly in ether, and reduces Fehling's solution, but is not affected by yellow mercuric oxide.

Potassium phenylhydrazine is prepared in a manner similar to and resembles the sodium compound (Abstr., 1886, 1025). A. J. G.

A Physical Peculiarity of α-Triphenylguanidine. By H. Giraud (*Bull. Soc. Chim.*, **46**, 505—506).—This substance, prepared from diphenylthiocarbamide and aniline, melts at 143°, and readily remains in a state of superfusion. When cooled quickly, its viscosity increases, and it passes insensibly into the solid state without showing any indication of crystalline form. It is then transparent, very fragile, is powdered by a blow, crumbles under pressure, and adheres to the fingers like resin. When cooled to 60°, it contracts and cracks, but does not crystallise. When slowly heated, it softens gradually until it becomes fluid (but no distinct melting point can be observed), and it then changes to the crystalline state with evolution of heat; this change is instantaneous at 60°. In contact with a liquid, the amorphous form becomes opaque and then crystalline before dissolving, the change being more rapid the greater the solvent action of the liquid. In this case also there is a rise of temperature of 7° to 8°. L. T. T.

Thiocarbimides of Bibasic Aromatic Radicles. By O. Billeter and A. Steiner (*Ber.*, **20**, 228—232).—When an aqueous solution of the hydrochloride of an aromatic diamine is shaken with a solution of thiocarbonyl chloride dissolved in chloroform, a good yield of the corresponding thiocarbimide is obtained with meta- and para-bases, but falls to 10 per cent. of the theoretical quantity in the case of ortho-bases, the chief product being the corresponding monothiocarbamide.

Orthophenylene thiocarbimide, $C_6H_4(NCS)_2$, forms colourless needles or scales, melts at 59° (corr.), is very readily soluble, and combines with alcohol and ammonia to form compounds analogous to those obtained from the meta-derivative.

Metaphenylene thiocarbimide crystallises in colourless needles, melts at 53° (corr.), boils with partial decomposition above 250°, and is readily soluble in all ordinary solvents. Alcoholic ammonia converts it into metaphenylene dithiocarbamide (Abstr., 1883, 324); and metaphenylenedithiourethane, $C_6H_4[NC(OEt)\cdot SH]_2$, melting at 116°, is obtained by heating it with alcohol. When heated at 250° with finely divided copper, a small yield of the nitrile of isophthalic acid is obtained.

Paraphenylene thiocarbimide crystallises in long, lustrous needles, melts at 130° (corr.), and is less soluble than its isomerides. Under similar conditions, it yields paraphenylene dithiocarbamide, and paraphenylenedithiourethane melting at 197°.

Orthotoluylene thiocarbimide, [Me : NCS : NCS = 1 : 3 : 4], crys-

tallises in white scales, melts at 42° (corr.), and is extremely soluble. When heated with hydrochloric acid at 200°, it is mainly converted into the *monothiocarbamide*, $C_7H_6(NH)_2CS$, which forms scales melting at 285°; whilst by the action of alcoholic ammonia it yields the monothiocarbamide and ammonium thiocyanate.

Metatoluylene thiocarbimide crystallises in long, colourless needles, melts at 56° (corr.) and boils at about 300° with partial decomposition. By the action of ammonia and aniline, it yields metatoluylene dithiocarbamide and diphenyltoluylene dithiocarbamide respectively. *Metatoluylenedithiourethane* crystallises in small, white scales, and melts at 119—120°. When metatoluylene thiocarbimide is heated at 250° with finely divided copper, a compound melting at 140—141°, and probably the nitrile of β-xylidic acid, is obtained. W. P. W.

Trianisylarsine and its Derivatives. By A. Michaelis and L. Weitz (*Ber.*, **20**, 48—52).—*Trianisylarsine*, $As(C_6H_4{\cdot}OMe)_3$, is prepared by adding sodium (20 grams) to a mixture of bromanisoïl (50 grams) with arsenic chloride (30 grams), diluted with four times the volume of ether and a small quantity of ethyl acetate. It forms hard, transparent, colourless crystals, which, although cubic in form, do not belong to the regular system. It melts at 156°, and is readily soluble in benzene, sparingly in alcohol and ether. It unites less readily than triphenylarsine with chlorine and bromine, and the oxide $AsO(C_6H_4{\cdot}OMe)_3$ is only obtained in a pure state with difficulty.

Dianisylarsine chloride, $As(C_6H_4{\cdot}OMe)_2Cl$.—When trianisylarsine is heated with hydriodic acid (sp. gr. 1·56) and the oil formed is treated with aqueous soda, the crystalline dianisylarsine oxide, $O(C_6H_4{\cdot}OMe)_2$, is obtained, melting at 130°, which, when treated with hydrochloric acid, is converted into the chloride. The latter crystallises in long, thin, pale yellow needles, melts at 79—80°, and is very readily soluble in ether, less so in alcohol.

Anisylarsine dichloride, $AsCl_2{\cdot}C_6H_4{\cdot}OMe$, prepared by heating trianisylarsine with a large excess of arsenic chloride for 24 hours at 200°, is a colourless liquid, which can be distilled at 230° under 117 mm. pressure, but suffers partial decomposition when distilled at the ordinary pressure. Sodium hydroxide or carbonate converts it into *anisylarsine oxide*, $AsO{\cdot}C_6H_4{\cdot}OMe$, a colourless, crystalline mass. When the dichloride is cooled with ice-water and treated with chlorine, *anisylarsine tetrachloride*, $OMe{\cdot}C_6H_4{\cdot}AsCl_4$, is obtained as a viscous, yellow liquid, which dissolves in water with considerable development of heat, and is soon converted into *anisylarsenic acid*, $OMe{\cdot}C_6H_4{\cdot}AsO(OH)_2$. This forms hard, colourless crystals, sparingly soluble in cold water, readily soluble in alcohol. If quickly heated, it melts at 159—160°, but if slowly heated it loses water and is converted into an infusible *anhydride*, $OMe{\cdot}C_6H_4{\cdot}AsO_2$, which is reconverted into the acid by boiling with water. The silver salt is described.

Triphenetylarsine, $As(C_6H_4{\cdot}OEt)$, is prepared from bromophenetoïl, arsenic chloride, and sodium; it melts at 88—89°, and is readily soluble in ether.

Similar trianisyl compounds were prepared from phosphorus and

antimony trichlorides, but have not yet been obtained in quantity sufficient for investigation. A. J. G.

Organo-bismuth Compounds: Valency of Bismuth. By A. Michaelis (*Ber.*, **20**, 52—54).—The author has entered on a general investigation of the organo-bismuth compounds to ascertain if any undoubtedly pentavalent bismuth compounds can be obtained. The alkyl compounds are being investigated by Marquardt, whilst the author and Polis are working on the aromatic compounds. The results obtained so far, are that whilst trimethyl- or triethyl-bismuthine do not form additive compounds with bromine nor with ethyl iodide, substitution of halogen for methyl, &c., occurring, triphenylbismuthine unites with chlorine or bromine, to form stable and well characterised compounds, in which 1 atom of bismuth is united with 5 monovalent groups or atoms. The pentavalent nature of bismuth is thus rendered as certain as that of antimony.

A. J. G.

Triphenylbismuthine and its Derivatives. By A. Michaelis and A. Polis (*Ber.*, **20**, 54—57).—*Triphenylbismuthine*, $BiPh_3$, is prepared by boiling an alloy of bismuth and sodium (10 per cent.) with bromobenzene and a little ethyl acetate for 50 hours in a reflux apparatus. The product is filtered, the residue repeatedly extracted with benzene, and from the united liquids the benzene first distilled off, and then, under reduced pressure, the bromobenzene. The fused triphenylbismuthine left solidifies when cooled and stirred, and is purified by repeated crystallisation from hot alcohol. It forms colourless needles or tables which resemble the crystals of triphenylarsine and -stibine, and seem to be triclinic. It has a sp. gr. = 1·5851 at 20°, melts at 82°, is readily soluble in ether and light petroleum, sparingly in cold alcohol, and closely resembles triphenylstibine in its chemical properties, save that it is less stable. When gently heated with hydrochloric acid, it is completely decomposed into benzene and bismuth chloride. When treated with bismuth bromide in ethereal solution, a yellow precipitate, probably *phenylbismuthine dibromide*, $BiPhBr_2$, is obtained.

Triphenylbismuthine dichloride, $BiPh_3Cl_2$, is prepared by passing chlorine gas on to the surface of a solution of triphenylbismuthine in light petroleum cooled with ice, as long as a white precipitate forms. It crystallises in thick prisms, melts at 140°, is readily soluble in benzene, sparingly in ether and cold alcohol, and is not decomposed by concentrated hydrochloric acid.

Triphenylbismuthine dibromide, $BiPh_3Br_2$, is prepared by mixing solutions of its components in light petroleum; it forms long, pale-yellow prisms, melts at 119°, and is readily soluble in benzene, sparingly in ether and alcohol. Both the bromide and chloride are decomposed by hydrogen sulphide, triphenylbismuthine being regenerated with separation of sulphur. A. J. G.

Synthesis of Phenaceturic Acid. By E. Hotter (*Ber.*, **20**, 81—85).—When glycocine, dissolved in as little water as possible, is

treated with sodium hydroxide and phenylacetic chloride and then with hydrochloric acid, a compound separates which, after drying and extraction with ether, dissolves in alcohol or water, and crystallises in the groups of white laminæ characteristic of phenaceturic acid. The yield is small. *Ethyl phenaceturate*, $C_{10}H_{10}NO_3Et$, crystallises in long broad prisms, melts at 79°, and is readily soluble in hot alcohol, less soluble in warm ether and benzene, insoluble in carbon bisulphide.

Copper phenylacetate, $(C_8H_7O_2)_2Cu$, is soluble in hot alcohol, and crystallises in small nodular masses consisting of radiating deep-green needles. W. P. W.

Phenylamidopropionic Acid obtained from the Decomposition of Proteïds. By E. Schulze and E. Nägeli (*Zeit. physiol. Chem.*, **11**, 201—206).—One of the authors has previously shown (Abstr., 1883, 1122) that one of the products of the decomposition of proteïds by means of hydrochloric acid is a substance with the properties and composition of phenylamidopropionic acid, and that the same substance, probably again the result of the decomposition of proteïds, can be obtained from the germinating seeds of certain plants (Abstr., 1882, 189).

This substance is very similar to the amido-acid prepared synthetically by Erlenmeyer and Lipp (Abstr., 1882, 971), and called by them phenyl-α-amidopropionic acid or phenylalanine. This opinion is held because by dry distillation both acids yield the same decomposition products, namely, carbonic anhydride, phenyllactimide, and phenylethylamine. Still there are certain differences between them. The acid obtained from proteïds and plants crystallises from warm concentrated aqueous solutions in shining plates, from dilute solutions in slender, white needles, containing water of crystallisation; whilst phenylalanine crystallises from hot water in prisms free from water, and from aqueous alcohol in shining plates. The melting point of the former acid is 275—280°, of the latter 263—265°. The copper salt of the latter contains 2 mols. H_2O, that of the former is free from water. Some of these differences might be explained on the supposition that the acid obtained from proteïds and plants is not so pure as that prepared synthetically. This would not, however, account for the difference of melting point. The optical examination of these substances led to the elucidation of this point. Phenylalanine prepared synthetically is optically inactive, whilst that obtained from proteïds and plants is active. In many pairs of isomerides, one of which is optically active, the other inactive, it is found that other differences, for instance, of solubilities and melting points, occur (see Abstr., 1886, 373). It is therefore concluded that the acid obtained from proteïds and plants is an optically active modification of phenyl-α-amidopropionic acid or phenylalanine. This conclusion is supported by the fact that tyrosin giving its typical microscopic appearances, and Piria's and Hoffmann's reactions, can be obtained from both acids by the two methods described by Erlenmeyer and Lipp. W. D. H.

Reduction of the Phthalic Acids. Constitution of Benzene. By A. Baeyer (*Ber.*, **19**, 1797—1810).—An account of the theoretical portion of this paper will be found in the March number of the Transactions (A. K. Miller, Trans., 1887, 208—215).

When tere- and iso-phthalic acids are reduced with sodium amalgam with the aid of heat, they both yield tetrahydro-acids, no intermediate dihydro-acid being formed; no reduction takes place in the cold. Phthalic acid, on the other hand, is reduced by sodium amalgam, slowly in the cold, more readily when warmed, to dihydrophthalic acid. The author explains this difference of behaviour on the assumption that only those double affinities (taking Kekulé's formula) can be reduced which belong to carbon-atoms in combination with carboxyl.

It is remarkable that the partly reduced acids behave towards bromine like unsaturated compounds; dihydrophthalic and tetrahydroisophthalic acids each take up two atoms of bromine. The dibromide of tetrahydroterephthalic acid yields a hydroxy-acid, from which by the action of bromine, a compound identical with tetrabromocatechol was obtained. Tetrahydroterephthalic acid has therefore the constitution—

$$[H{\cdot}COOH : H : H : H{\cdot}COOH : H_2 : H_2 = 1 : 2 : 3 : 4 : 5 : 6].$$

Tetrahydroterephthalic acid is prepared by boiling for 20 hours 5 grams of terephthalic acid, dissolved in the smallest amount of aqueous soda, and gradually adding 4 per cent. sodium amalgam (500 grams). It dissolves in 120 parts of boiling water, and separates on cooling in small prisms. It melts above 300° and sublimes. The silver salt is amorphous. The methyl salt is obtained as an oil which has the odour of fennel, and solidifies to very large prisms melting at 39°; its solutions have a blue fluorescence. When the ethereal solution of the salt is treated with sodium ethoxide, a rose-coloured transient precipitate is formed, similar to that obtained from ethyl succinosuccinate. When tetrahydroterephthalic acid is heated with hydriodic acid (b. p. 127°) for six hours at 240°, it is converted into *hexahydroterephthalic acid*, $C_8H_{12}O_4$. This is less soluble than the tetrahydro-acid, from which it is also distinguished by its stability towards potassium permanganate. It melts at about 295°, and sublimes. The *methyl salt* melts at 58°; its solution has no fluorescence.

Tetrahydroisophthalic acid is prepared by boiling 2 grams of isophthalic acid for two to three days with sodium amalgam. It dissolves readily in hot water, from which it crystallises in needles melting at 199°. The *silver salt* is amorphous; the *methyl salt* is an oil.

The author confirms the statement of Graebe and Born (*Annalen*, **142**, 345), that dihydrophthalic acid cannot be further reduced by sodium amalgam. It is best prepared by boiling phthalic acid with sodium amalgam; the yield is quantitative.

Dibromohexahydroterephthalic acid, $C_8H_{10}Br_2O_4 + H_2O$, is formed when 10 grams of tetrahydroterephthalic acid is shaken with 100 grams of a 5 per cent. ethereal solution of bromine, left for some time, and the ether poured off. This is repeated with fresh bromine solution until almost all the acid has dissolved. The united solutions

are decolorised with sulphurous acid and extracted with soda. The *methyl salt* crystallises from ether in large prisms, melting at 73°. The acid has about the same solubility in water as tetrahydroterephthalic acid; it is not decomposed when the solution is boiled for a short time. Warm soda solution decomposes it with formation of a *dihydroterephthalic acid*, $C_8H_8O_4$. When the dibromo-acid is treated with silver oxide, an acid is obtained, probably a dihydroxyhexahydroterephthalic acid.

According to Kekulé's formula, the two bromine-atoms and hence also the hydroxyl-groups, would both have the ortho-position:—

[H·COOH : H_2 : H_2 : H·COOH : HBr : HBr = 1 : 2 : 3 : 4 : 5 : 6].

This position of the hydroxyl was proved by treating the dihydroxy-acid with bromine; tetrabromocatechol was obtained, which gave an intense blue coloration with ferric chloride.

Dry hydrophthalic acid combines readily with bromine (1 mol.), yielding dibromotetrahydrophthalic acid. The acid is subjected in small portions to the action of bromine-vapour, the product freed from excess of bromine, dissolved in soda, filtered, and acidified. The oil is exhausted with ether, and distilled in a vacuum; it solidifies to well-formed rhombohedra (compare Graebe and Born, *loc. cit.*).

N. H. M.

Action of Potassium Hydroxide on Mixed Alkyl Bisulphides. By R. Otto and A. Rössing (*Ber.*, **20**, 189—191).—When an alcoholic solution of ethyl phenyl bisulphide is warmed with small quantities of alcoholic potash until the reaction is complete, the following compounds are obtained:—Ethylsulphinic and benzenesulphinic acids, ethyl mercaptan and phenyl bisulphide; the latter is formed by the oxidation of the potassium phenylmercaptide first formed.

W. P. W.

Action of Sulphurous Anhydride on Benzene. By C. E. Colby and C. S. McLoughlin (*Ber.*, **20**, 195—198).—When 100 grams of benzene and 35 grams of aluminium chloride, placed in a reflux apparatus, are treated with sulphurous anhydride until absorption of the gas is complete, then heated until hydrogen chloride ceases to be evolved, and the product, after cooling, poured into water, *diphenylsulphoxide*, Ph_2SO, is obtained, which crystallises from xylene in small, transparent crystals, which seem to be triclinic. It melts at 70—71°, and is readily soluble in alcohol, ether, acetic acid, and benzene, sparingly soluble in cold light petroleum. When oxidised with potassium permanganate, it yields diphenylsulphone, and when reduced with sodium, diphenyl sulphide is obtained. The same compound can be prepared by the action of thionyl chloride on benzene. For this purpose, 50 grams of benzene and 16 grams of thionyl chloride, placed in a reflux apparatus, are treated in the cold with successive quantities of aluminium chloride until hydrogen chloride ceases to be evolved; the product, after heating for half an hour, is poured into water, and the diphenylsulphoxide purified by crystallisation.

When equivalent quantities of diphenylsulphoxide and sodium nitrate are dissolved in sulphuric acid, and the two solutions mixed and heated at 100°, three nitro-compounds appear to be formed:—(1) Gericke's dinitrosulphobenzide, melting at 163° (*Annalen*, **100**, 211); (2) an oil not yet further examined; and (3) *dinitrodiphenylsulphoxide*, $(C_6H_4NO_2)_2SO$, which forms yellow, indistinct, microscopic crystals, melts at 116°, and is soluble in alcohol, readily soluble in ether, benzene, acetic acid, and carbon bisulphide. W. P. W.

Action of Potassium Hydroxide on Phenylenemetadiphenylsulphone. By R. Otto and A. Rössing (*Ber.*, **20**, 185—189).—Since ethylidenediethylsulphone and ethylidenediphenylsulphone are not attacked by alcoholic potash at 140° (*Ber.*, **19**, 2814), whilst ethylenediphenylsulphone readily yields benzenesulphinic acid and phenylsulphonethyl alcohol (Abstr., 1885, 261), the authors have examined the behaviour under like conditions of a disulphone of a third class, phenylenemetadiphenylsulphone, and find that the products of the action are benzenesulphinic acid and diphenylsulphonephenyl ether, $2C_6H_4(SO_2Ph)_2 + 2KOH = 2PhSO_2K + (C_6H_4SO_2Ph)_2O + H_2O$.

Diphenylsulphonephenyl ether, obtained by heating phenylenemetadiphenylsulphone with alcoholic potash at 160—170°, crystallises in small white feebly lustrous needles, melts at 69—70°, and is readily soluble in alcohol, ether, and benzene, insoluble in water. It can be volatilised unchanged only when carefully heated in small quantities, and distils above 200°. When heated with concentrated aqueous ammonia, no change occurs. Sodium amalgam in alkaline solution reduces it to benzene, benzenesulphinic acid, and a crystalline compound, which yields a bromo-derivative crystallising in large rhombic tables melting at 54—55°.

Ethylenediphenylsulphone when treated with an excess of concentrated aqueous potash, yields benzenesulphinic acid, and a small quantity of a compound possibly polymeric with diphenylsulphonethyl ether are obtained. W. P. W.

Synthesis of Carbazole. By A. Goske (*Ber.*, **20**, 532—534).—The author has succeeded in effecting the synthesis of carbazole from thiodiphenylamine. When this base is heated with an excess of metallic copper for two hours in an atmosphere of coal-gas, and the product afterwards distilled, a distillate is obtained which consists of carbazole; the yield amounted to 60 per cent. of the weight of the thiodiphenylamine employed. The synthetical carbazole melts at 238°, and gives the characteristic compound with trinitrophenol. Bearing in mind Bernthsen's synthesis of thiodiphenylamine from catechol and orthamidophenylmercaptan (this vol., p. 245), the constitution of carbazole must be represented by the formula—

$$<^{C_6H_4}_{C_6H_4}>NH\ [NH = 2, 2'].$$ W. P. W.

Action of Hydroxylamine on Diketones. By F. Münchmeyer (*Ber.*, **20**, 228).—The compound $OH{\cdot}N : C(C_6H_4{\cdot}NMe_2)_2$ melts at 233°, and not at 98—99° as previously stated (Abstr., 1886, 877).

W. P. W.

Naphthoic Acids. By Å. G. Ekstrand (*Ber.*, **20**, 219—226).—The compound obtained by the reduction of dinitro-α-naphthoic acid (m. p. 265°) with hydrogen sulphide in ammoniacal solution, to which the provisional formula $COOH{\cdot}C_{10}H_5 : N_2 : O_2$ was ascribed (Abstr., 1886, 948), contains sulphur either as an impurity or in combination. The purest specimen gave figures corresponding with the formula $C_{33}H_{18}N_6SO_6$; owing to its sparingly soluble and uncrystallisable nature it is impossible to decide whether the substance analysed was free from admixed sulphur, although none could be extracted by carbon bisulphide. If stannous chloride dissolved in aqueous potash is employed as the reducing agent, a compound is obtained resembling the preceding in its appearance, infusibility, and insolubility in alcohol.

Dinitro-α-naphthoic acid, probably $[NO_2 : NO_2 : COOH = 1' : 4' : 1]$, melting point 218°. When nitro-α-naphthoic acid (m. p. 239°) is nitrated with red fuming nitric acid, three dinitro-acids are obtained, of which two, melting at 205° and 265°, have been previously described, whilst the third melts at 218° and is formed in very small quantity. It is very soluble in alcohol, from which it is obtained in hard, deep yellow, rhombic crystals, $a : b : c = 0{\cdot}9731 : 1 : 1{\cdot}4424$, whilst from water it crystallises in slender needles. The *ethyl* salt crystallises in long, hard, yellow needles melting at 129°; the *calcium* salt, with 7 mols. H_2O, crystallises in thin, lustrous, broad, yellow needles, and is readily soluble in water. When reduced with tin and hydrochloric acid, the dinitro-acid is converted into the hydrochloride of an *amidonaphthostyril*, $NH_2{\cdot}C_{10}H_5{<}\begin{matrix}NH\\CO\end{matrix}{>},HCl$, which melts at a high temperature, and crystallises in long, bright yellow needles, sparingly soluble in cold water.

α-Naphthamidoxime, obtained together with α-naphthamide by heating an alcoholic solution of α-naphthonitrile and hydroxylamine in molecular proportions, crystallises in large laminæ, melts at 148—149°, and is readily soluble in alcohol, acetic acid, and benzene, soluble in water and insoluble in light petroleum. The *hydrochloride* crystallises after a long time in stellate aggregates of needles, and melts at 160°; the *platinochloride* forms long, prismatic, yellow needles. When heated at 100° with acetic anhydride, and the product treated with water, α-naphthamidoxime is converted into *α-naphthazoximethenyl*, $C_{10}H_7C{<}\begin{matrix}NO\\N\end{matrix}{>}CMe$; this crystallises from alcohol in long, colourless needles and melts at 36°. *α-Naphthoyl-α-naphthamidoxime*, $C_{10}H_7{\cdot}C(NH{\cdot}CO{\cdot}C_{10}H_7) : N{\cdot}OH$, obtained by heating α-naphthamidoxime and α-naphthoic chloride in molecular proportions at 100°, crystallises in small, slender needles, and melts at 228°; it is insoluble in alcohol and hydrochloric acid.

β-Naphthamidoxime, prepared in manner similar to the α-compound, forms lustrous scales, melts at 150°, is soluble in alcohol, and is

gradually decomposed by boiling water. The *hydrochloride* forms long needles, melts at 178°, and is very soluble in water. *β-Naphthazoximethenyl* crystallises in large scales, melts at 87°, and is soluble in alcohol. *β-Naphthazoximnaphthenyl*,

$$C_{10}H_7\cdot C\lessgtr\begin{matrix}NO\\N\end{matrix}\gtrless C\cdot C_{10}H_7,$$

obtained by heating β-naphthoic chloride and β-naphthamidoxime in approximately molecular proportions, crystallises in broad needles or scales, melts at 175°, and is almost insoluble in alcohol.

W. P. W.

α- and β-Naphthenylamidoxime. By E. Richter (*Ber.*, **20**, 227).—The author has independently arrived at results which confirm those of Ekstrand (preceding Abstract); *acetyl-α-naphthenylamidoxime* melts at 129°. *Acetyl-β-naphthenylamidoxime* melts at 154°; the *benzoyl*-derivative melts at 179°; the *ethyl* salt melts at 74—75°. Ethylidenenaphthenylamidoxime melts at 121—122°.

W. P. W.

Chloronaphthalenesulphonic Acids. By P. T. Cleve (*Ber.*, **20**, 72—75).—1 : 4′ *Chloronaphthalenesulphonic acid*, $C_{10}H_6Cl\cdot SO_3H + 2H_2O$, obtained by diazotising the amido-acid corresponding with α-nitronaphthalenesulphonic acid, crystallises in colourless tables readily soluble in water. A chlorosulphosulphonic acid,

$$C_{10}H_6Cl\cdot SO_2\cdot C_{10}H_6\cdot SO_3H,$$

is also formed in this reaction, this yields an insoluble amorphous potassium salt. *Potassium chloronaphthalenesulphonate* crystallises in lustrous needles; the *sodium* salt forms thin scales; the *silver* salt forms thin tablets sparingly soluble in water; these salts are anhydrous. The *barium* salt with 2 mols. H_2O is a sparingly soluble, indistinctly crystalline powder. The *ethyl* salt melts at 46°, and crystallises in large, monoclinic prisms, $a : b : c = 1{\cdot}6785 : 1 : ?$; $\beta = 68°\ 58'$, which show distinct pleochroism. The *chloride* forms triclinic crystals resembling hexahedra, melts at 95°, and is soluble in chloroform; the *amide* crystallises in lustrous scales, melts at 226°, and is sparingly soluble in alcohol.

1 : 4 Chloronaphthalenesulphonic acid (Abstr., 1883, 595) can be prepared by diazotising naphthionic acid. The *ethyl* salt melts at 104° and crystallises in large, thin, monoclinic tables, $a : b : c = 1{\cdot}32807 : 1 : 1{\cdot}12623$; $\beta = 80°\ 59'$. The *chloride* melts at 95°, and crystallises in triclinic forms; the *amide* melts at 187°.

α-Chloronaphthalene-β-sulphonic acid (probably 1′ : 2) is prepared by diazotising the amido-acid from the author's β-nitronaphthalenesulphonic acid (this Journal, 1877, i, 469); it crystallises in colourless rhombic tables and is readily soluble in water. The *potassium* salt forms very thin, glistening tables sparingly soluble in cold water; the *barium* salt, with 1 mol. H_2O, is a sparingly soluble, crystalline powder. The *ethyl* salt melts at 111°, is soluble in chloroform, readily soluble in hot alcohol, and crystallises in well characterised monoclinic forms; $a : b : c = 0{\cdot}43067 : 1 : ?$; $\beta = 86°\ 45'$, the crystals being either long prisms almost quadratic in section, or thick tables. The *chloride*

forms small scales, melting at 114—115°; the *amide* forms thin scales, melts at 216°, and is soluble in alcohol. W. P. W.

Brönner's β-Naphthylaminesulphonic Acid. By S. Forsling (*Ber.*, **20**, 76—81).—Brönner's *β-naphthylaminesulphonic acid*, $NH_2 \cdot C_{10}H_6 \cdot SO_3H + H_2O$, obtained by the action of ammonia on β-naphtholsulphonic acid at 180°, crystallises in colourless laminæ of silky lustre, and is very sparingly soluble in water, the solution having a blue fluorescence. The *potassium* salt with 1 mol. H_2O forms long, white needles, and is soluble in cold water to the extent of 1 in 40° to 45°; the *ammonium* salt with 1 mol. H_2O forms broad, white needles, and when heated at 180° gives off the whole of its ammonia; the *sodium* salt with 2 mols. H_2O forms white needles, and dissolves to the extent of 1 in 40 in cold water; the *silver* salt with 1 mol. H_2O is an indistinctly crystalline powder. The *barium* salt with 6 mols. H_2O crystallises in long, white needles, and requires 450 parts of cold water for its solution; the *calcium* salt with 6 mols. H_2O crystallises in laminæ, and dissolves in 225 parts of cold water; the *magnesium* salt with 6 mols. H_2O crystallises in laminæ or broad needles. The crystals of all these salts have a silky lustre, dissolve sparingly in water, and give solutions showing blue fluorescence. The *lead* salt with 2 mols. H_2O is very sparingly soluble in water; the *zinc* salt with 4 mols. H_2O forms well-characterised, microscopic crystals, and is sparingly soluble in water; the *copper* salt with 4 mols. H_2O forms microscopic needles, is very sparingly soluble in water, and has a mosaic gold colour which changes to red in the anhydrous salt. The corresponding diazonaphthalenesulphonic acid, $C_{10}H_6N_2SO_3$, a yellow microcrystalline powder, yields, by Sandmeyer's reaction and subsequent treatment with phosphoric chloride, the chloride of Arnell's β-chloronaphthalenesulphonic acid melting at 110° (Abstr., 1886, 555), from which ε-dichloronaphthalene, melting at 136°, is obtained by distillation with phosphoric chloride. The *amide*, $C_{10}H_6Cl \cdot SO_2NH_2$, crystallises in needles and melts at 183—184°.

W. P. W.

Some Essential Oils. By P. Soltsien (*Chem. Centr.*, 1886, 936—937).—An examination of *Oleum citri*, *Oleum bergamottæ*, and *Oleum cort. aurantiorum dulcium*. These oils were prepared specially and were therefore pure. The author has examined them with Heppe's copper butyrate reaction and also various turpentines (Abstr., 1885, 1163); he finds that it is of little value, as the action depends on the age of the oil. He also re-examined the bromination of the oils, and confirms Wallach's statements in the main. G. H. M.

Isomeric Camphols and Camphors. By A. Haller (*Compt. rend.*, **104**, 66—68).—Camphol from madder, discovered by Jeanjean, crystallises from light petroleum in hexagonal plates similar to the crystals of the other camphols. Borneo camphol is similar to the others, but its rotatory power, though equal in amount, is opposite in direction. Its derivatives, however, correspond in rotatory power and other properties with the derivatives of other camphols. Cam-

phol from amber crystallises from light petroleum in the ordinary form, but differs from the other camphols in its rotatory power and its behaviour with bromine. When treated with bromine, it yields a buttery product, which contains a small quantity of a dextrogyrate monobromocamphor melting at 75°, but the greater part of the product melts below 50°. The corresponding camphoric acid also differs from that derived from other camphols, since it melts at 202° and is less soluble in water.

The author's investigations show that all camphols are chemically identical, and differ only in their action on polarised light. The camphols from madder, valerian, N'gai, and Bang-Phien have the same molecular lævorotatory power, $[\alpha]_D = -37°$, and the corresponding camphors are identical with that from fever-few (*matricaire*). The camphor from *Dryabalanops camphora* has a rotatory power equal in amount but opposite in direction. Its derivatives are, however, identical with those from the other camphols. Camphol from amber is mainly a racemic camphol mixed with a dextrogyrate borneol.

C. H. B.

Carveol, Borneol, and Menthol. By R. Leuckart (*Ber.*, **20**, 114—116).—The author gives the name *carveol* to an alcohol, $C_{10}H_{15}\cdot OH$, which he has obtained by reducing carvole with sodium and alcohol. It is a thick liquid, has a characteristic odour quite different from that of carvole, and boils at 218—220°. The acetate and benzoate are liquid. With phenyl cyanate, even in the cold, it yields *carvyl phenylamidoformate*, $NHPh\cdot COO\cdot C_{10}H_{15}$. This compound forms small needles, easily soluble in alcohol, sparingly so in ether, and melts at 84°. Borneol similarly forms *bornyl phenylamidoformate*, $NHPh\cdot COO\cdot C_{10}H_{17}$, crystallising in needles soluble in boiling alcohol and melting at 133°. Menthol, under similar circumstances, yields *menthyl phenylamidoformate*, $NHPh\cdot COO\cdot C_{10}H_{19}$, which crystallises in silky needles soluble in boiling alcohol and melting at 111°. No corresponding compounds are obtainable from carvole, camphor, or bromo-camphor, which seems to point to the absence of a hydroxyl-group in the latter substances. At higher temperatures, reaction takes place between carvole and phenyl isocyanate; carbonic anhydride is evolved, and diphenylcarbamide is among the products of the reaction.

L. T. T.

Bornylamine. By R. Leuckart and E. Bach (*Ber.*, **20**, 104—114).—When small quantities of camphor (not more than 4 grams should be used in each operation) are digested with two and a half times their weight of ammonium formate in sealed tubes at 220—240°, carbonic anhydride, carbonic oxide, ammonium carbonate, and a syrupy mass are produced. The latter distils at 290—300°, and yields a compound of the formula $C_{11}H_{19}NO$, which crystallises in glistening scales, melts at 60—61°, and is easily soluble in alcohol and ether. When digested with aqueous hydrochloric acid, it yields a crystalline base, *bornylamine*, $C_{10}H_{19}N$, which melts at 158—160°, boils at 199—200°, and is easily volatile in steam. It resembles camphor in physical properties, smell, and volatility at ordinary temperatures, &c. It is very sparingly soluble in water, easily so in alcohol and ether, is a strong base, and forms easily soluble salts, the aqueous solutions of

which have an acid reaction. Its vapour-density is 5·5. It is lævorotatory, a 12·5 per cent. solution showing a rotation of $[\alpha]_D = -18° 35' 41''$. The *hydrochloride*, $C_{10}H_{19}N,HCl$, forms small, white needles melting with decomposition at 280°. An aqueous solution of the hydrochloride, on long-continued boiling, undergoes partial decomposition, depositing camphene. The *platinochloride* forms golden-yellow scales, the *acid sulphate*, $C_{10}H_{19}N,H_2SO_4$, rhombic plates. *Formobornylamine*, $C_{10}H_{18}N{\cdot}COH$, is obtained by the action of anhydrous formic acid on the free base, or of sodium formate on the hydrochloride. It forms glistening scales melting at 61°. This substance is identical with the original substance formed by the action of ammonium formate on camphor, and described above. *Acetobornylamine*, $C_{10}H_{18}NAc$, obtained by dissolving the base in acetic chloride, crystallises in colourless scales melting at 141°. *Benzobornylamine*, similarly prepared, crystallises in colourless scales which melt at 131°. *Bornylcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{17}$, is formed by boiling potassium isocyanate with bornylamine hydrochloride. It crystallises in colourless needles, which melt at 164°, and are easily soluble in alcohol and water. When an ethereal solution of bornylamine is allowed to act on methyl isocyanate, *methylbornylcarbamide*, $NHMe{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{17}$, is formed; it crystallises in scales melting at 200°, and is soluble in water and alcohol. *Bornylphenylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{17}$, similarly obtained, forms silvery needles, easily soluble in hot alcohol, sparingly in cold alcohol and ether, insoluble in water. It melts with decomposition at 248°. *Bornylphenylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_{10}H_{17}$, formed from phenylthiocarbamide and the free base, crystallises in colourless needles melting at 170°.

The authors believe bornylamine to be isomeric and not identical with camphylamine, described by Goldschmidt (Abstr., 1886, 249 and 557).

The authors have also succeeded in obtaining bornylamine, although in very small quantities, by the reduction of camphoroxime by sodium amalgam. From this fact, and from its method of formation from camphor, they (accepting the ketone-formula of camphor as the most probable one) ascribe to bornylamine the formula $C_8H_{14}<\begin{matrix}CH_2 \text{——}\\ CH(NH_2)\end{matrix}>$. They believe camphylamine to be very closely related to and probably only a position-isomeride of bornylamine.

The authors have also obtained from carvole a corresponding *carvylamine*, which is now being investigated. L. T. T.

Active Principles of Asclepias Currassavica, A. Incarnata, and Vincetoxicum Officinale. By C. Gram (*Chem. Centr.*, 1886, 735).—These three Asclepiadeæ contain a glucoside which the author calls *Asclepiadin*. In the aërial parts of *Asclepias currassavica* the easily decomposed asclepiadin of Harnack was found; this appears to be identical with the asclepin of Feneulle. The asclepiadin isolated by the author is easily soluble in water, sparingly soluble in alcohol; it is easily converted into the less active asclepin. Only asclepidin, and no asclepin, could be obtained from the root of *Vincetoxicum officinale*. The asclepin which is prepared from *Asclepias tuberosa* by Keith and

Co. consists of a mixture of asclepiadin, asclepin, and asclepion; the latter has the composition $C_{20}H_{34}O_3$; it melts at 104°, and is contained in *Asclepias syriaca* and in *Vincetoxicum*. The asclepiadin which is prepared by Parke, Davis, and Co., from *Asclepias tuberosa*, contains asclepin and a small quantity of a substance which has a tetanic action. G. H. M.

Conversion of Pyrroline into Pyridine-derivatives. By G. Ciamician and P. Silber (*Ber.*, **20**, 191—195).—Weidel has shown (Abstr., 1886, 56) that Hofmann's bromopyridine, which is identical with that prepared synthetically from pyrroline, is a β-derivative; with a view to confirm this result and to determine the position of the carbon-atom introduced into the molecule when pyrroline is converted into halogenated pyridine-derivatives by the action of chloroform (Abstr., 1881, 826), bromoform (Abstr., 1882, 1214), or methylene iodide (Abstr., 1886, 367), the authors examined the action of benzal chloride on pyrroline. When these substances are heated with sodium ethoxide in molecular proportions at 160—170° for six hours, a non-basic substance, which has not been further examined, and phenylpyridine agreeing in all its properties with the β-compound prepared by Skraup (Abstr., 1883, 1013), are obtained. The introduced carbon-atom therefore takes up the β-position in the pyridine molecule, the relationship between the bases being best expressed by the formulæ

$$NH<\begin{matrix}CH:CH\\CH:CH\end{matrix}> \text{ and } N<\begin{matrix}CH\cdot CR\\CH:CH\end{matrix}>CH.$$

W. P. W.

2 : 6 Dimethylpyridine Platinochloride. By T. Liweh (*Ber.*, **20**, 66).—A reinvestigation of the crystalline form of this salt has entirely confirmed Groth's statement (Abstr., 1886, 558) as to its isomorphism with picoline platinochloride. The following faces were observed: $\infty\breve{P}\infty$, ∞P, $\infty\breve{P}\infty$, $0P$, $\breve{P}\infty$, $-2\breve{P}2$, $+2\breve{P}2$ (monoclinic).

Oxidation of Symmetrical Trialkylpyridines. By S. Altar (*Annalen*, **237**, 182—201).—The formation of lutidinemonocarboxylic acid from β-collidine has been described by Voigt (Abstr., 1885, 812). The acid is most readily purified by precipitation from an alcoholic solution by platinum chloride. The *platinochloride*,

$$(C_8H_9NO_2)_2,H_2PtCl_6 + 4EtOH,$$

crystallises in thick prisms, which effloresce on exposure to the air, and change in colour from deep red to orange. At the ordinary temperature, the salt loses 2 mols. alcohol; at 120°, all the alcohol is expelled, and the anhydrous salt melts at 221°. By decomposing an aqueous solution of the platinochloride with sulphuretted hydrogen, the *hydrochloride*, $C_8H_9NO_2,HCl + H_2O$, is obtained in microscopic needles which are freely soluble in water. The free acid melts at 153°, and dissolves freely in water and alcohol; it crystallises with $\frac{1}{2}$ mol. H_2O. All the salts of the acid are soluble. As lutidine monocarboxylic acid yields α-γ-lutidine on distillation with lime, this acid may be regarded as *α-γ-dimethyl-picolinic acid*.

Ethyl dihydroisopropyllutidinedicarboxylate yields ethyl lutidinedicarboxylate on oxidation, and also when the ethereal solution is treated with dry hydrogen chloride.

When oxidised with potassium permanganate, parvoline, $C_5NH_2EtMe_2$, yields methylethylpyridinecarboxylic acid, $C_5NH_2EtMe{\cdot}COOH$. The platinochloride of this acid forms red crystals, which melt with decomposition at 194—195°.

The preparation of picolinedicarboxylic acid has been described by Voigt (*loc. cit.*). The crude product of the action of potassium permanganate on collidine is concentrated, and mixed with hydrochloric acid, when picolinedicarboxylic acid is slowly deposited. The precipitate is dissolved in ammonia and reprecipitated from the hot solution by hydrochloric acid. The pure acid melts at 274° with decomposition. It crystallises in slender needles, and is sparingly soluble in water. As picolinedicarboxylic acid is also formed by the oxidation of parvoline, the acid may be regarded as α-methyllutidinic acid, $COOH{\cdot}C_5NH_2Me{\cdot}COOH$. It is identical with Böttinger's uvitonic acid. W. C. W.

Quinolinedisulphonic Acid and its Derivatives. By W. La Coste and F. Valeur (*Ber.*, **20**, 95—104).—The best method of formation of the mixture of ortho- and meta-quinolinesulphonic acids is to heat 1 part of quinoline with $3\frac{1}{2}$ parts of fuming sulphuric acid at 170°. The reaction is then complete in one hour. The acids are best separated by means of their mercury salts, that of the ortho-acid being easily soluble, that of the meta-acid insoluble, in cold water. The authors, differing from O. Fischer and Bedall (Abstr., 1882, 869), find the ortho-acid to be sparingly, the meta-acid easily soluble in water.

The pure ortho-acid on sulphonation gives the same two disulphonic acids previously described by La Coste and Valeur (Abstr., 1886, 628). It is thus clear that the meta-acid yields only one disulphonic acid, and that this is identical with one of the two obtainable from the ortho-acid. The authors have examined some of the derivatives of α-quinolinedisulphonic acid. The *potassium* salt, $C_9NH_5(SO_3K)_2 + 3\frac{1}{2}H_2O$, crystallises in silky, white needles. *α-Quinolinedicyanide*, $C_9NH_5(CN)_2$, was obtained by the dry distillation of a mixture of the above potassium salt and potassium cyanide. It crystallises in short, grey needles, insoluble in water, sparingly soluble in ether, benzene, and chloroform, readily so in acids and alkalis; it melts at 220—222°. *α-Quinolinedicarboxylic acid*, $C_9NH_5(COOH)_2 + H_2O$, obtained by saponifying the dicyanide with soda, crystallises in needles which melt at 268—270°, and are soluble in alcohol, ether, chloroform, and boiling water. α-Hydroxyquinolinesulphonic acid (Abstr., 1884, 629) forms both normal salts and basic salts, in the latter, the phenolic hydrogen is also replaced. Both series of salts are crystalline, and mostly contain water of crystallisation; several of each series are described by the authors. Attempts to obtain oxidation products from this hydroxy-acid resulted almost uniformly in the total destruction of the compound, but in one case, with alkaline permanganate, a small quantity of a pyridinedicarboxylic acid was formed, which

seemed to be identical with the acid obtained by Hoogewerff and van Dorp by the oxidation of quinoline. L. T. T.

Quinoline-red. By A. W. Hofmann (*Ber.*, **20**, 4—20).—This substance was patented by Jacobsen (*Ber.*, **15**, 2646), who obtained it by heating quinoline with benzotrichloride and zinc chloride at 120—130°; the zinc chloride may be omitted if a higher temperature is employed. The yield is only about 5 per cent. of the quinoline used. As the quinoline recovered from the manufacture gives scarcely any of the red dye when again treated in like manner, it seemed probable that some constituent of the crude quinoline was essential to the formation of the dye. Experiments were therefore made with quinaldine and with isoquinoline. With mixtures of quinaldine and quinoline (eq. mols.) a yield of only $1\frac{1}{2}$ per cent. of the red was obtained, but when isoquinoline was substituted for quinoline the yield rose to 9 to 12 per cent. The dye thus obtained, although showing very great resemblance to quinoline-red, yet differs from it in several particulars; the two, therefore, are possibly isomeric.

Isoquinoline-red, $C_{26}H_{19}N_2Cl$, is obtained by heating quinaldine and isoquinoline (eq. mols.) with benzotrichloride and zinc chloride. The dye is formed far more readily than with quinoline. It crystallises in monosymmetric prisms, terminated by pyramids; $a : b : c = 0{\cdot}9783 : 1 : 1{\cdot}3651$, $\beta = 54°\ 24'$. By transmitted light, the crystals are deep crimson, in reflected light they appear reddish-brown with greenish-yellow, metallic lustre. It is soluble in water, alcohol, acetic acid, and phenol, insoluble in ether, carbon bisulphide, and benzene. The aqueous and alcoholic solutions are crimson with a strong yellowish-red fluorescence; the solutions dye wool and silk bright rose with some indication of yellow fluorescence; the colour is not fast. The dye prepared from quinoline crystallises invariably in slender needles, and in colour is pure red without metallic lustre; the solutions are crimson with a slight violet tint; the same violet tint is observable in wool or silk dyed with quinoline-red. The absorptive spectrum of both dyes in alcoholic solution consists of two bands in the green and bluish-green, but the bands of quinoline-red are narrower and more intense than those of isoquinoline-red. The platinochlorides, $(C_{26}H_{19}N_2Cl)_2,PtCl_4$, are obtained as scarcely crystalline precipitates, insoluble in water, alcohol, and hydrochloric acid; that from quinoline red is violet-red in colour, whilst the iso-compound is pure crimson.

As no difference has as yet been detected in the chemical behaviour of the two modifications, the term quinoline-red refers to both in the reactions and derivatives described. When treated with zinc and hydrochloric acid, quinoline-red is quickly decolorised with formation of a leuco-base, which has, however, not yet been further investigated. When the reduction is effected by heating with alcoholic ammonium sulphide in sealed tubes for 8 to 10 hours at 200°, benzyl mercaptan and a new base of the formula $C_{19}H_{14}N_2$ are obtained. This base crystallises in plates of golden lustre, melts at 231°, and sublimes at a higher temperature without decomposition; it is insoluble in water, sparingly soluble in ether, benzene, and cold alcohol, more readily in

carbon bisulphide, and readily in phenol. It shows feeble basic properties; the hydrochloride crystallises in colourless needles.

When heated with hydrochloric acid or when oxidised, quinoline-red yields benzaldehyde; as in the reaction with ammonium sulphide, the group introduced in the form of benzotrichloride is again eliminated.

When quinoline-red is distilled with zinc, a mixture is obtained from which a base, $C_{17}H_{15}N$, was isolated. This is crystalline, melts at 86—86·5°, and yields a sparingly soluble crystalline platinochloride.

Reviewing the evidence deducible from the formation and reactions of quinoline-red, the author considers that it must be represented either by $C_9NH_6{\cdot}CPhCl{\cdot}C_9NH_5Me$ or by $C_9NH_6{\cdot}CPhCl{\cdot}CH_2{\cdot}C_9NH_6$, but there is not yet sufficient grounds to decide which of the two formulæ is correct. A. J. G.

Combination of Quinaldine with Formamide. By P. T. Cleve (*Ber.*, **20**, 76).—When equivalent quantities of quinaldine and formamide are mixed together, a white crystalline mass, readily soluble in alcohol, ether, and chloroform, is at once obtained. The compound $C_9NH_6Me{\cdot}C(OH){\cdot}NH_2$ forms radiating groups of needles, melts at 76°, and is decomposed by water; when heated in a sublimation apparatus, oily drops are obtained, which soon become crystalline.

W. P. W.

1, 3 Dimethylquinaldine and its Derivatives. By G. Panajotow (*Ber.*, **20**, 32—42).—1, 3 *Dimethylquinaldine*, $C_9NH_4Me_3$ [Me_3 = 2′ : 1 : 2], is prepared by the condensation of metaxylidine with paraldehyde and concentrated hydrochloric acid. It crystallises in nearly colourless, monoclinic prisms or in small plates, melts at 146°, boils without decomposition at 260° under a pressure of 719 mm., and volatilises readily with steam. It has the characteristic odour of quinoline, is insoluble in water, readily soluble in alcohol, ether, and light petroleum. The *sulphate*, $C_{12}NH_{13},H_2SO_4 + H_2O$, forms small, white needles; the *hydrochloride*, $C_{12}NH_{13},HCl$, also crystallises in needles; the *nitrate* forms transparent, triclinic prisms; the *platinochloride*, $(C_{12}NH_{13})_2,H_2PtCl_6$, crystallises in orange-yellow needles; the *picrate* forms long, yellow needles, melting at 185°. The *methiodide*, $C_{12}NH_{13},MeI + H_2O$, crystallises in small, yellow needles.

Tetrahydrodimethylquinaldine, $C_{12}NH_{17}$, is formed by the reduction of the above base with tin and hydrochloric acid; it is an oil boiling between 200° and 250°, and, like tetrahydroquinaldine, gives the characteristic red colour when treated with dilute nitric acid; the platinochloride, $(C_{12}NH_{17})_2,H_2PtCl_6$, forms orange-coloured plates.

Nitro- 1, 3-*dimethylquinaldine*, $C_9NH_3Me_3{\cdot}NO_2$, is the only nitro-derivative obtained in the nitration of the base; it forms long, white needles, melts at 92°, and is readily soluble in ether and chloroform. The platinochloride has the formula $(C_{12}H_{12}N_2O_2)_2,H_2PtCl_6 + 3H_2O$. *Amidodimethylquinaldine*, $C_{12}NH_{12}{\cdot}NH_2$, obtained by reduction of the nitro-compound, crystallises in yellow plates.

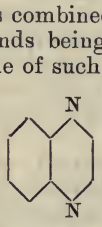
1, 3 *Dimethylquinaldinesulphonic acid*, $C_9NH_3Me_3{\cdot}SO_3H$, prepared by the action of pyrosulphuric acid on the base, crystallises in small, yellow needles, and does not melt up to 260°. The barium salt crys-

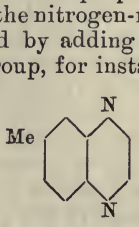
tallises with 3 mols. H_2O in silky needles, sparingly soluble in water. In order to ascertain the position of the sulphonic group in this substance, the author endeavoured to synthesise a corresponding or identical acid by condensation from Jacobsen and Ledderboge's metaxylidinesulphonic acid (Abstr., 1883, 593); he finds, however, that no condensation occurs with paraldehyde. This unexpected result would seem to indicate that the constitution of this metaxylidinesulphonic acid is not that given by its discoverers [$Me_2 : SO_3H : NH_2 = 1 : 3 : 4 : 6$], but that it is the 1 : 3 : 5 : 6 acid, as this latter constitution not only agrees with the non-formation of a quinaldine, but also brings the formation of the acid into the general rule that the sulphonic group when introduced into an aromatic amide does not assume the meta-position relatively to amidogen.

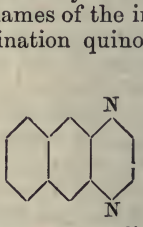
Dimethylquinolinecarboxylic acid, $C_9NH_4Me_2{\cdot}COOH$ [$Me_2 : COOH = 1 : 2' : 3$], is obtained by oxidation of 1 : 3 dimethylquinaldine with chromic mixture. It crystallises in small, white needles, cannot be fused without decomposition, but can be sublimed in small quantity in long, lustrous needles; it is sparingly soluble in water and cold alcohol. The silver (with 1 mol. H_2O) and barium salts are described. The *platinochloride*, $(C_{11}H_{10}N{\cdot}COOH)_2,H_2PtCl_6 + 4H_2O$, crystallises in orange-yellow needles; the *picrate* melts at 221°. When distilled with lime, it yields orthomethylquinaldine.

Dimethylquinoline-α-acrylic acid, $C_9NH_4Me_2{\cdot}CH : CH{\cdot}COOH$ = [1 : 3 : 2′]. When 1, 3 dimethylquinaldine is heated with dry chloral for eight hours on the water-bath, the condensation product $C_{14}H_{12}NCl_3 + H_2O$ is obtained in small, yellow needles, melting at 108°, and readily soluble in ether, alcohol, benzene, and hot light petroleum. This is boiled with aqueous potassium carbonate in a reflux apparatus for 15 hours, and the potassium salt formed, is neutralised with hydrochloric acid, when dimethylquinoline-α-acrylic acid separates. The latter crystallises in small, yellow needles, which decompose at 180°; the decomposition product melts at 210°. A. J. G.

Nomenclature of the Quinoxaline Series. By O. Hinsberg (*Ber.*, **20**, 21—23).—The author suggests that whilst the whole group of substances containing the typical ring should be termed quinoxaline bases, it will be convenient to divide them into two subgroups. 1. The quinoxalines proper, in which only a single-ring group is combined with the nitrogen-ring, the names of the individual compounds being formed by adding the termination quinoxaline to the name of such ring group, for instance,—


Quinoxaline.


Toluquinoxaline.


Naphthaquinoxaline.

2. The azines, in which the nitrogen-ring is in union with two other rings, of these compounds, phenazine, $C_6H_4\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_6H_4$, is the first member, the higher members being named—

$C_6H_4\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_{10}H_6$, Naphthazine. $C_7H_6\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_{10}H_6$, Tolunaphthazine. $C_6H_4\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_{14}H_8$, Phenanthrazine.

&c. A. J. G.

Nitrotolylglycine and Oxydihydrotoluquinoxaline. By R. Leuckart and A. Herrmann (*Ber.*, **20**, 24—31. Compare Hinsberg, Abstr., 1886, 82, Plöchl, and also the authors, *ibid.*, 351).—The barium, ammonium, and lead salts of orthonitrotolylglycine (nitrotoluidoacetic acid) are described. The *ethyl* salt crystallises in broad, yellow needles, melts at 65°, and is readily soluble in benzene, light petroleum, &c.

Chlordihydrotoluquinoxaline, $C_7H_6\langle\begin{smallmatrix}NH\cdot CH_2\\N : CCl\end{smallmatrix}\rangle$, is prepared by heating oxydihydrotoluquinoxaline with phosphoric chloride at 140—150°; it forms colourless needles, melts at 77°, has a quinoline-like odour, and is insoluble in water, very readily soluble in alcohol, ether, benzene, and light petroleum. It has feeble basic properties. When heated with alcoholic potash, the chlorine-atom is displaced with formation of the *exthoxide*, $C_7H_6\langle\begin{smallmatrix}-NH\cdot CH_2-\\N : C(OEt)\end{smallmatrix}\rangle$. This crystallises in brittle, silky needles, melts at 67°, and is readily soluble in hot water, alcohol, ether, benzene, or light petroleum. The corresponding *methoxide* melts at 71°. When the chloride is heated in acetic acid solution with hydriodic acid at 240°, amongst other products a few drops of an oil of quinoline-like odour was obtained; this probably is dihydrotoluquinoxaline, but the amount was too small for investigation. A. J. G.

Conyrine Platinochloride. By T. Liweh (*Ber.*, **20**, 67—68).—The author has submitted synthetical conyrine platinochloride (Abstr., 1887, 160) to a crystallographic examination, and gives results which show that the crystals are precisely similar in form to those of the conyrine platinochloride obtained from natural conine.

W. P. W.

Hydrastine. By M. Freund and W. Will (*Ber.*, **20**, 88—95).—In this paper, the authors substitute the formula $C_{21}H_{21}NO_6$ for that previously ascribed to hydrastine (this vol., p. 174). They have examined the base *hydrastinine*, $C_{11}H_{11}NO_2 + H_2O$, obtained together with opianic acid when hydrastine is treated with oxidising agents. Hydrastinine forms white crystals, melts at 116—117°, fusion, however, occurring if it be kept at 100° for some time, and is soluble in benzene, ethyl acetate (these solvents produce a partial decomposition), light

petroleum, ether, and water; the aqueous solution is strongly alkaline and intensely bitter. Like cotarnine, of which it is the next lower homologue, hydrastinine crystallises from all solvents with 1 mol. H_2O; this, however, is not present in its salts. The *hydrochloride*, $C_{11}H_{11}NO_2,HCl$, crystallises in feebly coloured needles, melts at about 212° with decomposition, and is readily soluble in alcohol and water; the aqueous solution shows a feeble fluorescence, and is optically inactive. The *sulphate*, $C_{11}H_{11}NO_2,H_2SO_4$, forms yellow crystals showing a green fluorescence, and is soluble in alcohol. The *dichromate*, $C_{11}H_{11}NO_2,H_2Cr_2O_7$, crystallises in slender, golden-yellow needles, and is soluble in water. The *methiodide*, $C_{11}H_{11}NO_2,MeI$, crystallises in slender, yellow needles showing a vitreous lustre, and is soluble in alcohol and water. The *platinochloride*, $C_{11}H_{11}NO_2,H_2PtCl_6$, and the *aurochloride* form yellow crystals, whilst with potassium ferricyanide a compound crystallising in reddish-brown needles is obtained.

Hydrohydrastinine, $C_{11}H_{13}NO_2$, is formed when hydrastinine is reduced with zinc and hydrochloric acid. This base forms white crystals, melts at 66°, and is readily soluble in ether, alcohol, benzene, carbon bisulphide, ethyl acetate, and acetone; the picrate crystallises in yellow needles. The *hydrobromide*, $C_{11}H_{13}NO_2,HBr$, forms tufts of small, white needles, and, like the hydrochloride, is sparingly soluble in water.

Hydrastinic acid, $C_8H_7NO_4$, is obtained by boiling hydrastine with dilute nitric acid until potassium hydroxide no longer precipitates the product. The acid is crystalline, melts at 232° with decomposition, is soluble in alcohol and water, and resembles apophyllic acid (Abstr., 1881, 110) in its properties. The *silver* salt, $C_8H_6NO_4Ag$, crystallises in needles. W. P. W.

Action of Phosphorus Pentachloride on Substituted Formamides and on Piperidine-derivatives. By O. Wallach and F. Lehmann (*Annalen*, **237**, 236—260).—The hydrochloride of a base of the composition $C_8H_{14}N_2$ is obtained by adding phosphoric chloride to a solution of diethylformamide in chloroform. The resulting phosphorus oxychloride is distilled off under reduced pressure, and the residue kept at a temperature of 100° for two hours. On the addition of platinum chloride to the alcoholic solution of the product, the platinochloride, $(C_8H_{14}N_2)_2,H_2PtCl_6$, is precipitated. The intermediate product, $C_{10}H_{19}ClN_2$, previously described by Wallach (Abstr., 1881, 719) could not again be isolated.

Diethylformamide forms two platinochlorides of the composition $(NEt_2{\cdot}COH)_4,H_2PtCl_6$ and $(NEt_2{\cdot}COH)_2,H_2PtCl_6 + 2H_2O$.

Piperidine also forms two platinochlorides. When platinum chloride is added to a concentrated aqueous solution of piperidine hydrochloride, an anhydrous salt, $(C_5H_{11}N)_2,H_2PtCl_6$, is precipitated. But if this salt is recrystallised from boiling alcohol mixed with a small quantity of hydrochloric acid, orange, needle-shaped crystals containing 1 mol. of alcohol are obtained, $(C_5H_{11}N)_2,H_2PtCl_6 + C_2H_6O$. The anhydrous salt melts at 198—200°, the alcoholic salt at 191°, both with decomposition.

Ethyl piperidyloxamate, $C_5NH_{10}\cdot CO\cdot COOEt$, is obtained as a colourless, oily liquid, heavier than and insoluble in water, by boiling a mixture of piperidine and ethyl oxalate for several hours. The product boils at 288—290°. It is converted into the oxamide by ammonia. The *oxamide*, $C_5NH_{10}\cdot CO\cdot CONH_2$, is deposited from a hot aqueous solution in monoclinic prisms; $a:b:c = 0{\cdot}66182:1:0{\cdot}53426$, $\beta = 50°\ 53{\cdot}5'$. It is soluble in alcohol and melts at 126—127°, and is converted into the nitrile of piperidyloxamic acid, $NC\cdot CO\cdot C_5NH_{10}$, by the action of phosphoric anhydride.

Piperidyloxamic acid, $C_5NH_{10}\cdot CO\cdot COOH$, is conveniently prepared by adding a concentrated alcoholic solution of sodium ethoxide to an alcoholic solution of ethyl piperidyloxamate. The free acid is deposited in needle-shaped crystals on the addition of hydrochloric acid to the solution of the sodium salt. It dissolves freely in alcohol and chloroform, and melts at 128—129° with evolution of carbonic anhydride. Piperidyloxamic chloride is decomposed by distillation, yielding carbonic oxide and piperidyl carbamic chloride. The carbamic chloride boils at 237—238°, and is decomposed by warm water. With aniline it yields *phenylpiperidylcarbamide*,

$$C_5NH_{10}\cdot CO\cdot NHPh,$$

a white crystalline substance melting at 171—172°. *Dipiperidyl carbamide* melts at 42—43°, and boils at 296—298°. It is freely soluble in ether, alcohol, chloroform, and in acids.

Formopiperidide, $HCO\cdot C_5NH_{10}$, prepared by heating piperidylcarbamic acid in a flask with a reflux condenser, is a colourless liquid boiling at 222°. The aqueous solution reduces silver salts and Fehling's solution, and forms a crystalline double salt with mercuric chloride, $HCO\cdot C_5NH_{10},HgCl_2$.

The hydrochloride is precipitated in deliquescent needles when hydrogen chloride is passed into a solution of formopiperidide in absolute ether. If the hydrochloride is dissolved in a small quantity of water, and mixed with alcohol and platinum chloride, a crystalline platinochloride is deposited which has the composition

$$(C_5NH_{10}\cdot COH)_4,H_2PtCl_6,$$

and is analogous to that obtained from diethylformamide. A complicated reaction ensues when phosphoric chloride acts on formopiperidide. The authors suggest that piperidine and the amidochloride, $C_5NH_{10}\cdot CCl_2H$, are formed in the first instance. These substances react on each other, yielding the compound $CHCl(C_5NH_{10})_2$, which unites directly with platinum chloride to form the salt $(C_{11}H_{21}N_2Cl)_2,PtCl_4$. W. C. W.

Ptomaïnes. By H. Beckurts (*Arch. Pharm.* [3], **24**, 1041—1065). —The detection of poisonous alkaloïds in forensic and similar cases is greatly increased in difficulty owing to the formation of ptomaïnes from albuminoïd substances of animal or vegetable origin, more especially as the ptomaïnes in their general chemical reactions bear great resemblance to the vegetable alkaloïds. It has repeatedly occurred in criminal cases, that the two classes of compounds have

been confounded, even by experts. All the basic nitrogenous products which result from the action of bacteria, whether of disease or decomposition, must be considered as ptomaïnes; and perhaps also certain definite poisonous basic substances, the leucomaïnes, which according to Gautier are formed during life in man and the higher animals.

Until very recently, only ptomaïnes of unknown composition had been isolated, and in all cases by the methods of Stas-Otto and Dragendorff. It is mainly to Brieger's investigations during the past four years, that we are indebted for a more accurate knowledge of the composition of these compounds. (For Brieger's method see Abstr., 1885, 278.) From decomposing flesh, Brieger obtained neuridine, $C_5H_{14}N_3$, and neurine, $C_5H_{13}NO$. From decomposing fish he obtained a poisonous isomeride of ethylendiamine, possibly ethylidenediamine, $C_2H_4(NH_2)_2$, muscarine, $C_5H_{15}NO_3$, and the physiologically inactive gadinine, $C_6H_{17}NO_2$. Fully decomposed cheese yielded neuridine. Decomposing glue gave neuridine, dimethylamine, and a muscarine-like base, whilst rotten yeast gave dimethylamine only. As these compounds result from the action of bacteria on animal tissues, so Brieger showed that the same or analogous compounds were similarly formed in the human subject. In the earlier stages of decomposition, only choline was found. After three days, neuridine appeared in increasing amounts, whilst choline gradually disappeared, being replaced by trimethylamine. After fourteen days, neuridine had also disappeared. Later, there most commonly appeared cadaverine, $C_5H_{16}N_2$, and putrescine, $C_4H_{12}N_2$. With cadaverine is also found a substance of the same composition, called *saprine*, but differing considerably in its reactions. The bases choline, neuridine, cadaverine, putrescine, and saprine are physiologically indifferent; but after fourteen days' decomposition a new poisonous base, *mydaleine*, was obtained which seems to be a diamine. In human remains (heart, lung, liver, &c.), maintained at -9 to $+5°$ C. during four months, a new base, mydine, $C_8H_{11}NO$, was found, a strongly reducing agent, and a poisonous base, mydatoxine, $C_6H_{13}NO_2$, also the poisonous methyl-guanidine was isolated. O. Bocklisch, employing Brieger's method, obtained a large number of bases from decomposing fish. The bases so obtained were not poisonous, and attempts to separate the injurious compounds were unsuccessful. The fact that decomposition bacteria induce the formation of numerous basic substances from albuminoïd compounds, makes it highly probable that pathogenic bacteria possess similar properties. Thus, Koch, Nicati, and Rietsch have found poisonous ptomaïnes in cholera. In cultivations of typhus bacilla, a strongly basic poison, typhotoxine, $C_7H_{17}NO_2$, was obtained; and from tetanus cultivations a strong base, tetanine, $C_{13}H_{30}N_2O_4$, was obtained. The bases obtained by Brieger are either liquids of definite boiling point, or solid crystalline substances. The salts show the so-called general alkaloïd reactions, so that as a group the ptomaïnes cannot be separated from the alkaloïds. The non-poisonous ptomaïnes readily give rise to poisonous compounds; thus, cadaverine, which has been shown by Ladenburg to be pentamethylenediamine, is converted by rapid distillation of the hydrochloride into the poisonous

piperidine. Whilst the constitution of cadaverine has just been indicated, putrescine is either a dimethylethylendiamine or methyl-ethyl-methylendiamine; which of the two, further investigation must decide. The present methods of isolating the alkaloïds do not yield absolutely certain results, and further extended investigation is required. J. T.

Origin of Ptomaïnes. By C. Gram (*Chem. Centr.*, 1886, 647).—Although it cannot be denied that a part of the basic products (so-called ptomaïnes) occurring in most putrefying substances is formed by the putrefactive process itself, for instance, the poisonous sepsine found in putrid yeast, it is nevertheless possible that some of these substances may arise simply by reason of the chemical processes involved in the separation of these basic products.

The simple action of heating organic compounds with ammonia salts may give rise to basic products.

The author has for a long time tried in vain to obtain poisonous bases from putrid meat by Maas's method. On treatment with amyl alcohol, an important quantity of these bases was obtained from meat in various conditions of putrefaction, but they were all perfectly inert.

The hydrochloric acid derivatives after heating on a water-bath were also inert, but the lactic acid compounds under similar treatment showed decidedly poisonous properties. Similar observations were made with other bases obtained from putrid yeast free from sepsine.

This transformation of a non-poisonous into a poisonous product by comparatively simple chemical action led the author to study the change of choline into the trimethylvinylammonium base. According to Brieger, the latter poisonous product is a frequent constituent of putrid matter, and arises from the action of putrefactive microphytes on choline.

This same change can be effected by purely chemical means. The lactate of choline when heated, gives rise to a poisonous substance with muscarine-like action. Inasmuch as many researches have shown that choline is widely distributed throughout animal and vegetable organisms, and as it is moreover capable of being converted into a poisonous substance by simple chemical action, the author considers it necessary to conduct researches on ptomaïnes with more caution, and perhaps to regard with mistrust ptomaïnes possessing a muscarine-like action. J. P. L.

Diastase. By O. Loew (*Ber.*, **20**, 58).—A reply to Lintner (this vol., p. 166), in which the author reaffirms the utility of the method of purifying ferments with lead salts, provided due precautions are taken.

Physiological Chemistry.

Artificial Digestion. By A. Stutzer (*Zeit. physiol. Chem.*, **11**, 207—232).—From a large number of artificial digestion experiments on the various forms of fodder used by cattle, it was found that after the gastric juice has digested all it can, a certain amount of the remaining proteïd can be digested by means of an artificial pancreatic juice. The pancreatic extract was mixed with sodium carbonate solution, but equally good results were obtained whether the amount of sodium carbonate present was $\frac{1}{4}$, $\frac{1}{2}$, or 1 per cent. It was also found that the best results were obtained when the digestive fluid consisted of 25 c.c. of pancreatic extract to 75 of sodium carbonate solution, or rather that when less pancreatic fluid was added than indicated by this proportion, there was a slight diminution in the amount of proteïd digested; when more than a quarter of the digestive fluid consisted of the pancreatic fluid, there was no increase in the amount digested. In order to obtain trustworthy results, it was found that six hours was a sufficient length of time to expose (at a temperature of 37—40°) the fodder to the action of the digestive fluid: a longer exposure than this caused no further digestion. Tables are appended to the paper which give for 28 varieties of fodder, the total nitrogen, the amount of nitrogen combined as proteïd, the amount of nitrogen not present in proteïds, the amount of proteïd digestible in gastric juice, the amount indigestible in gastric but digestible in pancreatic juice, and the amount not digestible by either. W. D. H.

Place of Origin of Uric Acid in the Animal Organism. By A. B. Garrod (*Proc. Roy. Soc.*, **40**, 484—485).—In continuation of previous experiments on the formation of uric acid in the animal economy (Abstr., 1883, 876), it is here shown that uric acid is secreted by the kidney cell as ammonium urate, and that the traces of sodium urate ordinarily found in the blood result from the necessary absorption of the ammonium salt from the kidneys into the blood, in which it is subsequently converted into the sodium salt.

The daily quantity of uric acid secreted, expressed as a ratio of the body-weight, varies from 1 in 1,000,000 in some carnivorous mammalia to 1 in 85 in birds; in man it may be regarded as 1 in 120,000. The quantity contained in the blood has but little relation to that secreted by the kidneys. When the acid is absorbed from the alimentary canal, the blood becomes strongly impregnated with it, but if taken into the stomach, the secretion from the kidneys is not thereby increased. The proportion of acid found in different veins in the same bird is variable; but the quantity secreted daily by the kidneys is closely related to the quantity of nitrogenous food taken in the same time. V. H. V.

Albuminoïds of Human Milk and of Cows' Milk. By Biedert (*Chem. Zeit.*, **10**, 1460—1461).—Remarking on the useless-

ness of the method of determining albuminoïds in milk which depends on the precipitation with magnesium sulphate, it is shown that the filtrate from the magnesium sulphate precipitate (I) yields a precipitate (II) with acetic acid; the filtrate from this yields a precipitate (III) on boiling, and this filtrate gives a precipitate (IV) with tannin. With human milk, precipitate I = about 0·15—0·71 per cent.; II = 0·08—0·32; III, 0·02—0·08; IV, 0·05—0·32; with cow's milk I = 2·33—2·58; II, 0·04; III, none or an unweighable quantity; IV, 0·07—0·12. There is a decided difference between the two kinds of milk.

E. Pfeiffer remarks that no method can be considered trustworthy which professes to separate these different albuminoïds in milks; and relies on methods such as Ritthausen's, in which all albuminoïds present in the milk are precipitated at once. He, moreover, points out that not only human and cows' but also mares' and asses' milk have their characteristic albuminoïds (caseïns). D. A. L.

Poisonous Ptomaïne in Milk. By R. H. Firth (*Lancet*, **1**, 1887, 213—214).—An epidemic of attacks of violent purging and vomiting among the soldiers in the Punjab was traced to the use of certain milk. The residue of the suspected milk was found to be of sp. gr. 1·025; caseïn, 4·1; fat, 3·9; and sugar, 5·04 per cent. The dairy pans were found to be unwashed, and some emitted a repulsive odour; the weather at the same time was very hot. The milk was coagulated, filtered; the filtrate was neutralised and made feebly alkaline by potassium hydrate, and shaken with ether. On evaporating the ethereal extract, a crystalline residue of sickly odour and pungent taste was obtained. Given to men in small quantities, it produced nausea and headache. Given to dogs, in 15 minutes it produced violent purging and vomiting.

First, milk tested in a similar way gave negative results. Eight samples of milk were allowed to stand, and tested every 20 days. After two months, three of the samples yielded the same crystalline substance which produced the same symptoms when given to animals. This substance—which seems to be a ptomaïne—is evidently the result of decomposition. No specific organisms on which to fasten it—beyond some common forms of oidium and penicillium—were found. The name proposed for it is *lactotoxine*. W. D. H.

Nitrates in Animals and Plants. By W. Gossels (*Chem. Centr.*, 1886, 805—806).—The source of nitric acid in urine is very uncertain; it remains undetermined whether the nitrates come from the food or originate in the animal body. Differences appear to prevail in the individual classes of animals; thus, whilst with a flesh diet the urine of dogs is free from nitrates, human urine under the same circumstances contains nitrates. In the human subject, a portion of the nitrates—which are either formed in the body or proceed from the food—are not altered. This is confirmed by the experiments of Weyl (Abstr., 1885, 413).

The amount of nitric acid separated remains nearly constant, and undergoes no increase on adding potassium nitrate to the food.

Experiments on the action of uric acid showed that this changed the greater part of the potassium nitrate taken into other products, thus allowing only a small quantity to be secreted in the form of nitric acid. From this it may be concluded that a reduction process is going on in the body, the end-product of which is ammonia. G. H. M.

Hüfner's Reaction in Bile. By J. Marshall (*Zeit. physiol. Chem.*, **11**, 233—238).—Observations were made on the contents of the gall-bladders of 543 American oxen who had lived on prairie grass in the West, and on dried hay during the three days' journey to Pennsylvania. Of these specimens 295 had a yellow, 248 a green colour. Hüfner's reaction was given by 15·4 per cent. of the yellow specimens, and by 6·8 per cent. of the green: 22 per cent. in all. The sp. gr. of the bile was on the average 1·024; the minimum being 1·016, the maximum 1·037. The mean volume of the contents of the gall-bladder was 322 c.c.; the maximum being 730, the minimum 90 c.c.

The proportion of glycocholic to taurocholic acid in those specimens which gave Hüfner's reaction was 1 : 0·77; in those which did not give the reaction it was 1 : 33; and, in some cases, glycocholic acid was absent altogether.

The bile was mixed with hydrochloric acid and ether; the proportion of bile, acid, and ether being 100 : 5 : 30. It was then allowed to remain 24 hours in a cool place. In some cases crystallisation began almost immediately, but after a long time there was but little increase in the amount of crystallisation which occurred. To hasten crystallisation, instead of the ethyl ether used by Hüfner, light petroleum was found better. Benzene was also employed, but it was found that the crystals obtained by that means were badly formed, and impregnated with the biliary pigment.

The best and quickest method of obtaining glycocholic acid in colourless crystals is as follows:—A drop of hydrochloric acid is added to fresh bile; the mixture shaken and filtered; ethyl ether and hydrochloric acid are then added to the filtrate in the proportion above noted; the mixture shaken and allowed to remain. The crystals formed are collected on a filter, washed with water holding hydrochloric acid and ether in solution, and dried in the air. By recrystallisation they are obtained perfectly colourless. W. D. H.

Albumin in Normal Urine. By C. Posner (*Chem. Centr.*, 1886, 730—731).—When an excess of alcohol or tannin is added to a filtered urine in which the ordinary tests fail to detect albumin, a greater or less precipitate is thrown down under all conditions. In both cases, the precipitate must contain the whole of the albumin. The alcoholic precipitate, tested with the biuret reaction, with glacial acetic and concentrated sulphuric acids, and with gold chloride in formic acid solution, gives reactions which show that albumin is present in the urine. It is apparently serum albumin. G. H. M.

Mucin in Urine. By H. Citron (*Chem. Centr.*, 1886, 775).—Filtered urine often gives a precipitate with acetic acid which is insoluble in an excess of the reagent, and gives the reactions for albumin.

This is especially the case with the decomposed and alkaline urine of patients suffering from catarrh of the bladder. This precipitate is probably a decomposition-product of cellular tissue. A similar substance also occurs in true albuminous urine, or in urine which does not contain ordinary albuminoïds. This precipitate, when it does not consist of uric acid, must not be ascribed to mucin.

Mucin never occurs in undecomposed urine in cases of catarrh of the bladder, and only in the very slightest traces, if at all, when decomposition has occurred. G. H. M.

Physiological Action of Paraldehyde. By A. Bockal (*Chem. Centr.*, 1886, 622).—In opposition to Cervello, the author has found that paraldehyde acts as a stimulant before it acts as a hypnotic; the magnitude and duration of this stimulating action being in inverse ratio to the dose. During the period of excitation, the reflexes are increased, but they gradually subside with larger doses until they are altogether completely lost.

With toxic doses, the power of reflex action is lost so rapidly that the stimulating action as well as the original increase of reflex action pass unobserved.

Applied locally, paraldehyde acts similarly to chloroform and ether. Death is caused by paralysis of respiration, which may to a certain extent be counteracted by artificial respiration. In consequence of its vasomotor action, paraldehyde causes an increased secretion of urine. It is a powerful antidote to strychnine, for 10 times the fatal dose of strychnine may be administered to dogs that have previously received paraldehyde without any toxic effect. Strychnine, on the other hand, is not an antidote to paraldehyde. J. P. L.

Physiological Action of Methylal. By A. Mairet and Combemale (*Compt. rend.*, **104**, 248—250).—The experiments were made on guinea-pigs, cats, dogs, and monkeys. The results show that sleep is produced more rapidly by hypodermic injection or by inspiration of the vapour than by injection, but in the last case it is more persistent. The higher the animal in the scale, the more sensitive is it to the hypnotic action of the methylal. In large doses, methylal exerts a toxic action, and may cause death by producing inflammatory lesions of the different organs; but in doses of 0·25—0·5 gram per kilo. of body-weight the only symptom observed is deep sleep preceded by somewhat increased salivation; and if the slumber is very prolonged the temperature is slightly reduced. The methylal is rapidly eliminated from the system, and the heaviness which is apparent immediately on awakening rapidly passes away. C. H. B.

Butylchloral Hydrate and Chloral Hydrate as Antidotes for Strychnine and Picrotoxin. By E. Koch (*Chem. Centr.*, 1886, 811).—Butylchloral hydrate is useless as an antidote for strychnine poisoning; in picrotoxin poisoning, it behaves in the same way as chloral hydrate, both fail to overcome the treble minimum fatal dose of the poison. Picrotoxin is successfully used as an antidote against the narcosis of butylchloral hydrate and chloral hydrate. In spite of

many similarities, these two substances are very different in their mode of acting, not only quantitatively but also qualitatively.

G. H. M.

Action of Gaseous Poisons. By J. Belky (*Chem. Centr.*, 1886, 887—889).—By applying a spectroscope to the ear of a rabbit, the author has been able to observe during life the changes produced in the spectrum of the blood by various gaseous poisons. On ligaturing the base of the ear, the blood thus cut off from the general circulation loses its oxygen, and the spectrum of reduced hæmoglobin is developed. In poisoning by *carbonic oxide*, the fact of the formation of carboxy-hæmoglobin during life was ascertained.

In poisoning by *hydrocyanic acid*, the oxyhæmoglobin bands were well seen up to the moment of death, but a few minutes afterwards they were replaced by a single band, which was proved to be that of hæmoglobin, and not of the hydrocyanic acid compound examined by Preyer, by the fact that the spectrum of oxyhæmoglobin returned when the ear was plunged for a time into cold aërated water.

Nitrous oxide appears to have no different action from that of other inert gases. With *nitric oxide*, reduction of the oxyhæmoglobin occurred in 1½ minutes, the hæmoglobin band being visible at the moment of death. By interrupting the experiment when reduction was nearly complete, or by immersing the ear after death in aërated water, the oxyhæmoglobin bands returned. There was therefore no evidence of the formation of a compound of nitric oxide and hæmoglobin incapable of absorbing oxygen. Moreover, the blood did not become purple, as was the case with blood treated with nitric oxide after removal from the body.

Ammonia gas reduces the oxyhæmoglobin, and may therefore cause death by asphyxia, even when so dilute as to be respirable. By discontinuing the ammonia in time, oxyhæmoglobin is again formed.

Hydrogen sulphide reduces oxyhæmoglobin vigorously, but oxidation returns when the blood is exposed to air.

M. J. S.

Sausage Poisoning. By A. Ehrenberg (*Zeit. physiol. Chem.*, **11**, 239—256).—Sausages, the consumption of which had caused an epidemic of "sausage poisoning" in Würtemberg, were subjected to chemical investigation. Metallic poisons having been proved absent, Brieger's method (*Ptomaïne*, Berlin, 1885—6) was used for the isolation of bases the result of putrefaction; the following bases were separated and identified by their reactions, and by the analysis of their auro- or platino-chlorides: choline, neuridine, dimethylamine, trimethylamine, and methylamine. The injection of these bases or their chlorides into animals subcutaneously, or their administration by the mouth, caused no symptoms of poisoning. It is supposed that in the later stages of putrefaction the poisonous bases become broken up into these simpler but non-poisonous compounds. This is supported by the fact that if poisonous sausages are kept over a certain time, they lose their toxic properties. Or again, in certain cases where poisonous products are not obtained, this may be due to the fact that the methods of investigation which involve repeated evaporation with hydrochloric acid, may decompose the bases in question. On

distilling the sausages with fuming nitric acid, a distillate containing indole and skatole was obtained. Ammonia was also present.

Bacteriological investigation showed the presence of two forms of micrococcus, and a bacillus which rapidly liquefied gelatin. This bacillus was alone investigated. Sterilised preparations of blood, liver, lung, heart, and intestine, the materials out of which the sausages are chiefly made, were subjected to its action, the usual precautions against infection from other bacteria being taken. From blood, skatole, indole, and leucine were obtained after it had acted for ten days; from the liver, lung, and heart similarly treated, indole, butyric acid, choline, neuridine, dimethylamine, and trimethylamine were obtained. From the intestine, ammonia, choline, methylamine, dimethylamine, trimethylamine, and diethylamine were obtained. In control experiments in which no special bacillus was employed, but simply putrefaction allowed to take place, the same substances were formed, with the exception of diethylamine. As a result of the action of the bacillus on a nutritive medium, consisting of meat infusion to which peptone was added, trimethylamine, diethylamine, neuridine, and triethylamine were formed. In all the preceding cases, the bases obtained were injected into animals (guinea-pigs and rabbits), and in all cases with a negative result. If this bacillus is the cause of the formation of a poisonous base, it is necessary to investigate its action at different stages, for in the later stages of its action it seems to act destructively on the bases formed, or it may be here again that the methods adopted to obtain the bases themselves bring about the decomposition of the poison into the simpler non-poisonous compounds above mentioned.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Constituents of Bacteria. By L. Vincenzi (*Zeit. physiol. Chem.*, **11**, 181—183).—The experiments relate to *Bacillus subtilis*. A pure culture was obtained by Roberts' (*Phil. Trans.*, **164**) method. The fluid containing them was filtered through asbestos, the bacteria remaining on the filter were washed with water and 0·5 per cent. sodium hydroxide solution, digested with artificial gastric juice for 24 hours, washed free from peptones; finally they were washed with alcohol and ether, and dried.

In the cell-wall, which was all that remained after this treatment, no cellulose was found; but it was nitrogenous, yielding from 5·3 to 11·15 per cent. of nitrogen in different specimens, the amount seeming to depend on the different stages of growth of the bacteria. No opinion is expressed as to the nature of this nitrogenous substance.

W. D. H.

Behaviour of Micro-organisms in Artificial Mineral Waters. By J. Sohnke (*Chem. Centr.*, 1886, 699).—The author corroborates

previous observations as to the effect of carbonic anhydride on the micro-organisms present in water. Water thus impregnated suffers a constant diminution in the number of organisms possessing vitality. In spring water containing a number of organisms he found that from one-half to two-thirds were rendered inert, or incapable of reproduction, after the water had been impregnated with carbonic anhydride. J. P. L.

Source of Trimethylamine in Ergot of Rye. By L. Brieger (*Zeit. physiol. Chem.*, **11**, 184—185).—The presence of choline bases in *Secale cornutum* suggested that it might be the source of the trimethylamine found by Walz. The base obtained is undoubtedly choline; crystals of its aurochloride were obtained; these were prismatic, the prisms often grouped in stars. They contained 44·57 per cent. of gold (theory 44·45). This salt is decomposed at 264° (uncorr.). With platinum chloride, the platinochloride was also obtained. After removing the choline from the alcoholic extract of *Secale cornutum* by precipitation with alcoholic mercuric chloride and filtering, not a trace of trimethylamine was obtained by distilling the filtrate, so showing that it is under ordinary circumstances a decomposition product of choline. W. D. H.

Amount of Caffeïne in Various Kinds of Coffee. By B. H. Paul and A. J. Cownley (*Pharm. J. Trans.* [3], **17**, 565).—In estimating caffeïne in coffee beans, the best results have been obtained by the following method. The finely powdered coffee is mixed with moist lime, and percolated with alcohol. The residue left on evaporating the percolate is treated with water and a few drops of dilute sulphuric acid, filtered, and the filtrate exhausted with chloroform, which on evaporation leaves the caffeïne fit for weighing. By this method, the following results have been obtained with different kinds of unroasted coffee :—

Kind of coffee.	Percentage of caffeïne.
Coorg	1·10
Guatemala	1·18
Travancore	1·16
Liberian 1	1·20
Liberian 2	1·28

Roasted coffee contains about 1·3 per cent. of caffeïne, but this amount varies slightly. D. A. L.

Ash of Cinchona Bark. By D. Hooper (*Pharm. J. Trans.* [3], **17**, 545—546).—The average obtained from 300 estimations shows that barks cultivated in India contain over 3 per cent. of ash. Renewed and old natural barks are poorer, but never fall below 2 per cent. of ash. Young bark and branch bark gives as much as 4 per cent., and the leaves as much as 5 and 6 per cent. Natural crown bark, which grows at an altitude of 7000—8000 feet, is richer in ash than natural bark which grows at 5000—6000 feet, and the red is

richer than the ledger growing at 3000—5000 feet. The following analyses are of ashes from the bark grown on the Nilgiris, *C. officinalis* in the Dodabetta plantation, *C. succirubra* at a lower level at Naduvatam. The figures agree on the whole with those of Carles for American barks, except that no copper has been detected.

	Soluble in water.	Soluble in acid.	Insoluble.
C. officinalis, per cent. ..	27·33	66·92	5·75
C. succirubra, „ ..	24·46	69·94	5·60

	Insol. SiO_2.	Soluble SiO_2.	Al_2O_3.	Fe_2O_3.	Mn.	CaO.	MgO.
C. officinalis..	5·75	1·42	2·70	2·85	trace	32·7	2·07
C. succirubra.	5·60	4·40	4·24	3·21	—	32·8	2·52

	K_2O.	Na_2O.	CO_2.	SO_3.	P_2O_5.	Cr.
C. officinalis..	16·35	3·40	27·22	1·16	3·93	0·45
C. succirubra.	12·49	2·28	27·77	1·08	3·19	0·42

D. A. L.

Action of Mercurial Vapour on Leaves. By V. Jodin (*Ann. Agronom.*, **12**, 563—580).—The author has studied especially the influence of mercurialisation on respiration, and on the power of resistance to desiccation. Simple exposure of the leaf to an atmosphere which is in contact with a surface of mercury or of an amalgamated plate, is sufficient to excite the phenomena of mercurial poisoning. These are an increase at first in the respiratory power, due to a sort of stimulation, perhaps similar to that produced by electricity; after some time the respiratory power falls below that of a non-mercurialised leaf. As regards transpiration, the effect of mercurial vapour is to destroy in a very short time the resisting power of the leaf to desiccation, so that, for example, a leaf which normally takes 103 hours to lose half the total quantity of water which it is capable of losing by exposure to air, will, after mercurialisation, suffer the same amount of desiccation in 14 hours. A litre of air saturated with mercurial vapour at 20° contains at most 0·00071 gram of the metal, yet this quantity is sufficient to produce in a few hours the complete mercurialisation of 30 grams of fresh leaves. It is difficult to class this phenomenon amongst the chemical or mechanical phenomena hitherto recognised as physiological factors. J. M. H. M.

Direct Absorption of Nitrogen from the Atmosphere by Vegetable Soils. By Berthelot (*Compt. rend.*, **104**, 205—209).—The author has extended his researches (Abstr., 1886, 175, 736) to the case of vegetable soils.

The soils were placed in vessels of glazed earthenware, and in some cases were protected, in others exposed to air and rain, the rain-water being collected and analysed, and the amount of ammonia and nitric acid in the air being also determined. The results show that vegetable soils continually absorb nitrogen from the air, even when they are not supporting vegetation. The amount absorbed is in all cases very much greater than the quantity of nitrogen existing as ammonia or nitrogen

oxides in the air or rain. In fact the rain removes from the soil in the form of soluble nitrates considerably more nitrogen than it brings in the form of ammonia. At the same time, the amount of nitrogen absorbed is far greater in the case of soil exposed to rain than where the soil is protected, probably owing to the greater activity possessed by the nitrogen-absorbing organisms under the former conditions. In the majority of cases, a notable proportion of the absorbed nitrogen is converted into nitrates. C. H. B.

Analytical Chemistry.

Determination of Sulphur in Albuminoïd Substances. By W. Kochs (*Chem. Centr.*, 1886, 894).—Carius's method always gives low results, since even after heating for three hours at 200° the oxidation of the sulphur is not complete. Liebig's method, on the other hand, gives higher and concordant results. Since, however, albuminoïd substances free from ash are liable to produce too violent an evolution of gas, it is convenient to heat the substance with 10 parts of nitric acid of sp. gr. 1·4, and evaporate to dryness on the water-bath before fusing with potash and nitre. M. J. S.

Weil's Method for the Volumetric Estimation of Sulphides. By C. Friedheim (*Ber.*, **20**, 59—62).—The author states that this method is utterly untrustworthy, as copper sulphide when precipitated by hydrogen sulphide from ammoniacal copper solutions carries down copper oxide, and the copper sulphide has a great tendency to oxidise and redissolve. Under these circumstances, a correct result can only be obtained when the error in the one direction chances to equal that in the other. A. J. G.

Volumetric Estimation of Nitrous Acid. By A. G. Green and F. Eversheb (*J. Soc. Chem. Ind.*, **5**, 633—634).—In a previous communication (Abstr., 1884, 870), Green and Rideal described a process for the volumetric estimation of nitrous acid by means of aniline. Although the results obtained by this process are very accurate, it is somewhat lengthy, and requires too much care in manipulation to be generally available for technical purposes. In the modification described in the present paper, the authors have greatly simplified and shortened the operation by substituting normal for decinormal solutions. The advantage of this process is that most oxidisable substances which may be simultaneously present are not affected. In fact it is possible to estimate nitrites by this means under conditions which would entirely preclude an oxidation method. D. B.

Determination of Phosphorus in Steel and Iron. By C. Meineke (*Chem. Centr.*, 1886, 682).—By precipitating with molybdate

solution at not too high a temperature, the percentage of phosphorus in the ignited precipitate may be taken as 1·754. At higher temperatures the percentage is smaller, but can never exceed the above. There is no necessity to remove silica when determining phosphorus by this method in siliciferous iron. M. J. S.

Determination of Phosphoric Acid. By F. Bente (*Chem. Centr.*, 1886, 948).—On the occasion of a phosphoric acid determination, in which the precipitates with molybdate and magnesia respectively were allowed only 3 or 4 hours to form instead of 12, as was formerly the practice, low results were obtained. As no other cause for the deficiency could be assigned, the author thinks that the modern practice requires reconsideration. M. J. S.

Detection of Arsenic. By H. Hager (*Chem. Centr.*, 1886, 680—681).—The liquid to be tested is brought in contact with a plate of brass, when the presence of arsenic will be indicated by a grey deposit. Heavy metals, even iron, must be absent. Pure hydrochloric acid should be added until the liquid contains 5—15 per cent. of hydrogen chloride. If much arsenic is present, it is sufficient to put a few drops of the liquid on the brass plate and warm gently. After a minute or two the plate may be rinsed with water and examined. For minute traces, it is better to leave the drops on the plate in the cold, and examine from time to time without rinsing off. One part of arsenic in 80,000 will give a grey film in half an hour, 1 in 250,000 in an hour. If $1\frac{1}{4}$ hours elapse without any indication, arsenic may be considered to be absent.

If antimony is suspected, it is better to immerse a strip of brass in the liquid, and either warm (50—99°) or set aside for some hours at ordinary temperature. Arsenic gives a steel-grey to black film, antimony a light-grey. Held in a spirit lamp flame, an arsenic film becomes steel-blue and volatilises; antimony remains unchanged. If the deposit can be scraped off into a dry test-tube, add to it two drops of water, then 10 of nitric acid (30 per cent.). Arsenic will dissolve, antimony remain undissolved. M. J. S.

Use of Copper containing Arsenic for the Dearsenification of Hydrochloric Acid. Reinsch's Test for Arsenic. By H. Hager (*Chem. Centr.*, 1886, 772—773).—Copper foil used for the dearsenification of hydrochloric acid must be pure and its surface bright and free from dirt. Copper foil which has been already used for this purpose, may be scoured with sand to remove the film of arsenic, and again used. The fact that the copper usually contains traces of arsenic does not interfere with its use for the dearsenification of hydrochloric acid, since the arsenic exists in the form of an alloy which is not attacked by acid.

Before using copper foil for the qualitative detection of arsenic by Reinsch's method, it should be tested as follows:—A piece of perfectly bright foil is immersed in perfectly pure hydrochloric acid of 10 to 12·5 per cent., and allowed to remain for two hours; if at the end of that time it is still quite bright, it may be used for the detection of

arsenic; if the surface has become dimmed, the foil is of course rejected. The foil may contain traces of arsenic and still give no coloration with acid; in that case, it can be used both for the dearsenification of acid and for the qualitative detection of arsenic.

For the detection of arsenic in copper, Odling's method may be used. This consists in distilling the copper with hydrochloric acid and iron oxide or chloride; volatile arsenic chloride passes over and is found in the distillate.

A rapid and good test for arsenic in copper is to place a drop of ammonium hydroxide on a piece of bright metal, allow it to remain 30 minutes, wash off with water and dry with a cloth; then place a few drops of dilute acetic acid on the spot and allow to remain 10 minutes, again wash with water and dry with a cloth. If the copper contains traces of arsenic, a gray colour is seen where the ammonium has been. This is a very sure test. G. H. M.

Apparatus for Estimating Carbonic Anhydride and all similar Gases. By R. Bauer (*J. pr. Chem.* [2], **35**, 86—87).—Improvements in the form previously described (Abstr., 1884, 1216) with the object of rendering it less fragile.

Application of Allen's Nitrometer to the Estimation of Ammonium Carbonate in Spiritus Ammoniæ Aromaticus. B.P. By E. D. Gravill (*Pharm. J. Trans.* [3], **17**, 445).—For the purpose suggested in the title, the nitrometer is filled with mercury, 5 c.c. of spiritus ammoniæ aromaticus admitted, then gradually 5 c.c. of hydrochloric acid, and the volume of carbonic anhydride liberated is measured with the necessary precautions. D. A. L.

Estimation of Zinc as Pyrophosphate. By M. Bragard (*Chem. Zeit.*, **10**, 1605—1606).—The process described by Lösekann and Meyer (Abstr., 1886, 836) is identical with that given by Tamm (this Journal, 1871, 1214). The author states that it is more convenient to treat the zinc solution with the necessary quantity of ammonium chloride, acidify with hydrochloric acid, heat to boiling and, whilst hot, add the disodium phosphate until the reaction is alkaline. The liquid must be stirred all the time, care being taken to avoid rubbing the sides of the vessel; it is then boiled for two or three minutes and left at rest for 24 hours. The precipitate (without the filter-paper) may be ignited to fusion without suffering loss of pyrophosphate; but it is more convenient not to carry the ignition so far. The presence of filter-paper during ignition occasions loss owing to reduction and volatilisation of zinc. Many ways were tried to get rid of the paper; the best way is to remove as much of the precipitate as possible, then treat the filter with a saturated solution of ammonium nitrate, evaporate, ignite, &c. The precipitate is practically insoluble in water at 16°. D. A. L.

Determination of Cadmium and its Separation from Copper. By A. Kohner (*Chem. Centr.*, 1886, 813—815).—The author has examined the methods proposed for the estimation of cadmium and

its separation from copper. He concludes that the gravimetric determination of the sulphide is not accurate enough for anything but technical work; the volumetric method gives good results for amounts of cadmium sulphide between 0·07 and 0·6 gram. The determination as sulphate is fairly accurate for large quantities. The pyrophosphate method is quite untrustworthy, since the double phosphate is soluble in water (0·03 gram in 1000 c.c.) and very easily reduced during ignition. To obtain good results, the precipitate must be washed with the smallest possible quantity of water, dried at 100°, separated as completely as possible from the filter-paper, and what remains on the paper neglected. The precipitate, when washed with alcohol and ether and dried, has the composition $CdNH_4PO_4$.

The following is the best method for the separation of copper:—The solution of the two metals, freed as far as possible from free nitric and hydrochloric acids, is treated in an Erlenmeyer's flask in a water-bath with a concentrated solution of sulphurous anhydride. When the copper solution is nearly reduced, a little more sulphurous anhydride solution and a previously calculated amount of potassium iodide are introduced. If sufficient sulphurous anhydride is present, the slight yellow colour disappears on boiling. The excess of sulphurous anhydride is driven off and the copper iodide collected on a tared filter. The cadmium is precipitated from the filtrate by hydrogen sulphide and weighed as sulphate. This method requires the amount of copper present to be approximately known, since the presence of an excess of potassium iodide leads to errors. The separation of the two metals by sulphuric acid can under certain conditions give good results. The methods which require the addition of an organic substance to effect the separation are not to be depended on. G. H. M.

Estimation of Manganese. By R. W. Atkinson (*J. Soc. Chem. Ind.*, **5**, 365—367, and 467—468).—A detailed criticism of the methods in general use for the estimation of manganese. The old gravimetric method depends for its accuracy on attention to details combined with the recognition of the fact that the manganese dioxide first precipitated is impure, retaining both lime and zinc oxide when these are present in the original sample. Owing to the length of time occupied in the gravimetric method of estimating manganese, the use of Pattinson's volumetric process is strongly recommended by the author, although it is said to give results which are slightly below the truth, the difference being attributed to the incomplete oxidation of the manganese. Where accuracy is required, the gravimetric method in which the manganese is twice precipitated by bromine and ammonia, however tedious, is the only practical process. D. B.

Volumetric Determination of Manganese. By R. Schöffel and E. Donath (*Monatsh. Chem.*, **7**, 639—650).—When arsenious acid is added to a hot, neutral solution of potassium permanganate previously treated with a corresponding amount of zinc sulphate and some zinc oxide, the solution is quickly decolorised with formation of arsenic acid and manganese dioxide. The titration of the arsenious acid is carried out as follows:—300 c.c. of water is heated

to boiling and treated with 30 to 50 c.c. of a saturated solution of zinc sulphate together with some zinc oxide sludge; a known volume of permanganate solution is added, and then, drop by drop, the solution of arsenious acid until the permanganate is decolorised. The arsenious acid solution is prepared by dissolving 1·5 to 1·8 gram of the ordinary acid in 1 litre of water. The zinc oxide and sulphate must both be treated with permanganate before being used.

200 to 300 c.c. of water and 30 c.c. of a saturated zinc sulphate solution are heated to boiling; some zinc oxide sludge and a known volume of permanganate solution are added, and then gradually the manganese solution. The amount of permanganate must be such that the solution after addition of the manganese solution is still strongly coloured. It is again heated to boiling and titrated with the arsenious acid solution. Better results are obtained when zinc oxide is not added until before the titration with acid. When iron is present, as is often the case, it is necessary to add the zinc oxide as first described, otherwise the separation of the precipitate containing iron is not so quick.

The estimation of manganese in special cases is carried out as follows: 1 or 2 grams of the spiegeleisen or crude iron, &c., in the form of borings is dissolved by boiling with hydrochloric acid, diluted and filtered, and the solution boiled with an excess of potassium chlorate. The solution is made up to 200 or 300 c.c., and an aliquot part neutralised with sodium carbonate and treated with a slight excess of prepared zinc oxide. It is added to a mixture of 200 to 300 c.c. of water and 30 c.c. of saturated zinc sulphate solution previously boiled and then treated with a known amount of permanganate solution; it is boiled and the excess of permanganate titrated with arsenious acid.

In the case of manganese ores containing more than 40 per cent. of manganese, the amount taken is about $\frac{1}{2}$ gram. N. H. M.

Volumetric Estimation of Antimony in the Presence of Tin. By H. Giraud (*Bull. Soc. Chim.*, **46**, 504—505).—It is well known that whilst in neutral solutions antimony trichloride is oxidised by iodine, in very acid solutions the reverse reaction takes place. Stannic chloride is not thus reduced by hydriodic acid. The author makes use of this difference as a means of estimating antimony.

The mixed salts are converted into chlorides, dissolved in hydrochloric acid, and potassium chlorate added to convert them into perchlorides. The excess of chlorine is driven off by heat, and an equal volume of hydrochloric acid and an excess of potassium iodide then added. The iodine liberated is extracted with carbon bisulphide, and titrated with sodium thiosulphate. L. T. T.

Ferric Chloride as a Test for Organic Substances. By W. H. Ince (*Pharm. J. Trans.* [3], **17**, 461—462).—The author prepares a neutral ferrous chloride from cupric chloride by means of iron wire, and in the course of testing he converts this into ferric salt by adding bromine. The following reactions are obtained: I, being with

ferrous chloride; II, with addition of bromine; III, with addition of excess of bromine.

	I.	II.	III.
Gallic acid	faint blue	indigo	bleached
Tannic acid	colourless or faint blue-violet	blue-black	green to red
Pyrogallol	faint blue	ruby	ruby
Ammonium benzcate ..	colourless	reddish ppt.	no change
„ salicylate..	rose	violet	brown-red
Cinnamic acid	colourless	yellow-orange ppt.	no change
Sodium acetate.....	do.	ruby	no change
Morphine	do.	dirty-blue	yellow-white ppt.

D. A. L.

Precipitation of Dextrin by Iron. By H. A. Landwehr (*Chem. Centr.*, 1886, 954).—In opposition to Nasse, the author maintains the possibility of separating gum and glycogen from dextrin, by precipitating ferric oxide in the liquid; the two former being thrown down, and the dextrin remaining in solution. The precipitation by iron of the achroodextrin, obtained by Nasse from glycogen, proves its distinctness from ordinary dextrin. The insolubility of the precipitate in hydrochloric acid, and the difficulty of removing all the iron, however, renders this method for the determination of glycogen less convenient than the older one of Brücke.

The precipitation of glycogen or gum by ferric hydroxide appears to be due to a mechanical adhesion, as there is too much iron in the precipitate for a compound in molecular proportions. M. J. S.

Estimation of Fatty Acids in Soaps. By R. Bauer (*J. pr. Chem.* [2], **35**, 88—89).—The solution and decomposition is performed in the usual manner by warming 5 grams of the fresh soap covered with glycerol until the mixture is homogeneous; it is then treated with 100 c.c. of alcohol, and titrated with hydrochloric acid. An excess of acid is then added, and the layer of fat which separates transferred by means of a pipette to a clock-glass; the clock-glass is placed on a larger glass previously covered with a layer of fine glass pearls, and heated in an oven. The flask is washed out with a little light petroleum until free from fat. The glasses which had previously been weighed are then weighed with the fat. The percentage of free alkali is determined by estimating the carbonic anhydride before and after treatment with ammonium carbonate.

N. H. M.

Quantitative Estimation of Oxalic Acid in Urine. By O. Nickel (*Zeit. physiol. Chem.*, **11**, 186—200).—The methods of estimating oxalic acid in urine, proposed by Neubauer and Schultzen, were compared together, and found to give very varying results. The amount of variation was not constant, as the percentage of oxalic acid was sometimes higher by the one, sometimes by the other method.

Various modifications of both methods were also tried, but with equally unsatisfactory results. The variations seem to depend on the slight solubility of calcium oxalate in media in which it was formerly supposed to be insoluble, such as acetic acid, distilled water, and alcohol. There is also no certain method of separating calcium oxalate from the phosphate. No new method of analysis is, however, proposed. W. D. H.

Estimation of Fat. By M. Kretzschmar (*Chem. Zeit.*, **10**, 1556).—To avoid the inconvenience attached to the removal of the dried mass when using gypsum as the absorbing material in the estimation of fat in milk, the following modification is suggested. By means of a suitable mould, a square piece of tin-foil is pressed firmly in to the porcelain dish which is intended for use, the foil is made fast by turning down the projecting corners. The gypsum and milk are put in this, and when dry are easily lifted out and pulverised; the foil is cut up and put in the extraction apparatus along with the powder.
D. A. L.

Analysis of Oils. By L. Archbutt (*J. Soc. Chem. Ind.*, **5**, 303—312).—*Maumené's Test.*—In employing this test for the examination of rape and olive oil, the author found that without great care very discordant results might easily be obtained. He describes in detail the method he uses. From the results of a series of experiments made with a view of showing the effect of employing sulphuric acid of different strengths, it is inferred that there is no advantage in using weak acid on the ground of greater concordance in the results, the use of an acid of 97 per cent. strength being preferred. It appears best to allow the acid to drop slowly from the pipette into the oil.

The Elaïdin Test.—The author describes a method of preparing a reagent for this test, which gives perfectly concordant results, and which will keep for several days, whilst Poutet's solution rapidly undergoes change, and has always to be freshly prepared. From a series of trials made with a view to determine the best mode of applying this test so as to detect fraudulent admixtures, the author concludes (1) that the test must be made at a temperature not lower than 25°, and that the temperature must be uniform throughout the experiment; (2) that the length of time required for solidification is of far greater importance than the ultimate consistence of the elaïdin formed.

Iodine Absorption.—The author has made some experiments with rape oil, the results of which on the whole confirm those of Hübl, which were made on olive oil. He finds that in order to obtain the maximum absorption, it is necessary to add about twice the quantity of iodine actually absorbed, and to allow the solution to remain at least from 3 to 6 but not more than 24 hours before titrating.
D. B.

Distinction of Castor Oil from other Fatty Oils. By Finkener (*Chem. Zeit.*, **10**, 1500).—Shaking with alcohol, sp. gr. 0·829, at ordinary temperature (about 17·5°) yields turbid solutions with olive, sesame, linseed, cotton-seed, or rape oil, or with castor oil

mixed with these oils, whereas pure castor oil gives a clear solution. For testing purposes, 10 c.c. of the castor oil is poured into a 100 c.c. cylinder marked at 10 c.c. and 60 c.c. from the bottom, 50 c.c. of alcohol is added, the whole well shaken, and examined after being at rest two or three minutes; turbidity indicates the presence of at least 10 per cent. of other oils. Castor oil yields with sulphuric acid a substance soluble to a clear solution in 40 volumes of water, but this is the case even when it is mixed with 20 per cent. of olive or sesame oil; although these oils and other fatty oils yield milky solutions when treated in a similar manner. D. A. L.

Preserving Standard Tartar Emetic Solutions. By A. R. Miller (*J. Soc. Chem. Ind.*, **5**, 464).—It was found that by excluding the air from the solution it was possible to keep it for any length of time without decomposition taking place. D. B.

Opium Analysis. By C. M. Stillwell (*Amer. Chem. J.*, **8**, 295—308).—The method differs from those of Flückiger and Squibb in a number of details. The sampling must be very carefully conducted and the whole made homogeneous by rolling with the hands on a slab of glass, in case the opium is soft; but by grinding with or without additional drying if it be hard. About 10 grams of the sample is broken up with 100 c.c. of water in a beaker, and when completely disintegrated allowed to remain some hours; a few drops of sulphuric acid may be added. The solution is filtered and the residue washed with about 20 c.c. of water, then returned to the beaker, digested for some minutes with 30 c.c. of water, again filtered, and this process repeated twice more. The washings are first concentrated at a gentle heat on a water-bath, then the stronger solution is added and the whole evaporated to about 25 c.c. When cold, 5 c.c. of alcohol (sp. gr. 0·82) is added, and the whole transferred to an Erlenmeyer's flask, using 5 to 10 c.c. of wash water; 5 c.c. of alcohol and finally 30 c.c. of ether are added with gentle shaking; any precipitate that may form is to be disregarded, as it is removed afterwards, 4 c.c. of ammonia solution (sp. gr. 0·960) is added, the flask closed with a cork moistened with ether, and at once shaken until the morphine separates, when it is allowed to remain 12 hours.

The ethereal layer is decanted on to a small filter, the flask rinsed several times with 10 c.c. of ether without shaking, and these rinsings also decanted on to the filter; the aqueous portion is then filtered, the crystals removed from the flask, and the whole washed with morphiated spirit (1 part of strong ammonia and 20 parts of alcohol, the whole saturated with morphine, namely, 0·33 per cent.); secondly, with morphiated water (containing 0·04 per cent.), again with morphiated spirit; and finally twice with 10 c.c. of ether to remove all narcotine. The paper is dried at 100°. The mother-liquor and the first washings of ether and morphiated spirit are treated with 3 c.c. of ammonia in a closed flask, and again allowed to remain to make sure of the precipitation being complete. The chief impurity in the morphine so obtained is calcium meconate, and some organic matters insoluble in water and alcohol; the purification is effected by treating

the dried and weighed precipitate with hot alcohol of 95 per cent.; after removing the bulk of it to a beaker, the paper and residue, after thorough extraction with hot alcohol, are dried and weighed, thus giving the weight of the pure morphine. H. B.

Estimation of Quinine Sulphate. By G. Vulpius (*Arch. Pharm.* [3], **24**, 1022—1023).—The method described is identical with that given in the next Abstract.

Quinine Chromate in Analysis. By J. E. de Vrij (*Arch. Pharm.* [3], **24**, 1073).—4 grams of quinine sulphate is dissolved in 400 grams of boiling water; to this is added 1 gram of potassium chromate dissolved in a little water; after remaining some hours quinine chromate separates in anhydrous crystals of the composition $(C_{20}H_{24}N_2O_2)_2,H_2CrO_4$; it is soluble at 14° in 2733 parts of water, and at 16° in 2000 parts.

For the estimation of cinchonidine in quinine sulphate, 5 grams of the sulphate is dissolved in 500 grams of boiling water, 1·2 grams of potassium chromate dissolved in a little water added, and the whole allowed to remain until next day, when the quinine chromate is collected on a filter and washed. The mother-liquor and washings are heated with soda on a water-bath for some time, whereby the cinchonidine separates out in the crystalline form, and is collected, dried at 160°, and weighed. The author found in 5 grams each of three commercial samples, 0·197, 0·205, and 0·244 gram of cinchonidine respectively.

To determine the amount of pure quinine in the sulphate, 2 grams of the sulphate was taken and treated as above with 0·5 gram potassium chromate. The precipitated chromate was weighed, and this weight was increased by 0·05 gram for each 100 c.c. of mother-liquor and wash-water. From the total thus obtained, the amount of quinine is easily calculated. J. T.

Neutral Quinine Chromate. By O. Hesse (*Pharm. J. Trans.* [3], **17**, 585 and 665).—Recently De Vrij (preceding Abstract) recommended a process for estimating quinine in the sulphate, it was based on the formation of quinine chromate, which was washed, air-dried, and weighed as $(C_{20}H_{24}N_2O_2)_2,H_2CrO_4$. The author of the present communication now points out that the air-dried sample contains, in addition to the above, 2 mols. H_2O. It becomes anhydrous at 80°, at higher temperatures decomposes. In a note, the Editor of the above Journal points out that the dry salt rapidly absorbs moisture from the air, and attains the same weight it had before drying. For this and another reason, the large correction required for solubility, the method is not recommended.

In the second paper, it is shown that hydroquinine and cinchonidine, when present in quinine sulphate, cannot be correctly determined by De Vrij's chromate method, for although the neutral chromates of these two substances are more readily soluble than quinine chromate, yet they cannot be separated from the latter by crystallisation, as they crystallise out with the quinine chromate. In fact, where quinine

sulphate contains 8 per cent. or less of hydroquinine, the latter behaves exactly like quinine; whilst in the presence of 0·3 per cent. of cinchonidine, the mother-liquor from the quinine chromate yields a precipitate consisting not wholly of cinchonidine, as is supposed by De Vrij, but for the most part of a compound of seven molecules of cinchonidine with one molecule of quinine; also when the percentage of cinchonidine exceeds 0·3, the mother-liquor not only behaves in the same way, but a varying quantity of cinchonidine chromate crystallises with the quinine chromate. The mixture of chromates obtained on treatment with ammonia and ether yields the compound $C_{20}H_{24}N_2O_2,2C_{19}H_{22}N_2O$, which by crystallisation from hot dilute alcohol can be converted into large, brilliant, rhombohedrons of the formula $C_{20}H_{24}N_2O_2,7C_{19}H_{22}N_2O$. D. A. L.

Quinine Sulphate. By E. Jungleisch (*J. Pharm.* [5], **15**, 5—18).—A criticism of methods of assaying quinine sulphate, showing that the methods given in the Codex of 1884, after Kerner and others cited, are more or less unsatisfactory. J. T.

Detection of Rosaniline Salts and Sulphonated Rosaniline. By A. Liebmann and Studer (*J. Soc. Chem. Ind.*, **5**, 287).—Schiff's researches (*Compt. rend.*, **64**, 487) have shown that aldehydes give an intense violet coloration with a solution prepared by treating rosaniline salts with sulphurous anhydride. Schmidt (Abstr., 1882, 179) confirmed the general application of this reaction, and showed that acetone produced the same violet tint. The authors have successfully applied this reaction to the detection of aldehydes or acetone in the urine of persons suffering from diabetes. They have found that this property of the aldehydes and of acetone can be applied inversely for the detection of rosaniline salts and sulphonated rosanilines in dyes, wines, and lozenges. This test is exceedingly delicate, a distinct reaction with acetone being obtained, for instance, when cudbear is adulterated with only one-fortieth per cent. of rosaniline. D. B.

Detection of Acid Coal-tar Colours in Wine. By J. H. de Rego (*Chem. Centr.*, 1886, 842—843).—Girard's process in its original form fails to detect acid coal-tar dyes, but it can be used by filtering whilst the mixture is still acid.

The following method is very serviceable for red dyes, but not for others:—10 c.c. of the wine is nearly neutralised with a 5 per cent. potash solution; a saturated acid solution of mercuric acetate is added until the mixture is greenish, and it is then filtered. If the wine contains an acid dye, the filtrate will be coloured, and the colour will become more intense on adding hydrochloric acid; if otherwise, the filtrate will be yellowish, and will become paler with acid. A deep yellow filtrate, becoming red with hydrochloric acid, may be obtained from a pure wine if the process be varied.

A much more sensitive test is the following:—To 5 drops of the wine, if a strongly coloured Portuguese wine, or about 1 c.c. of any other wine, add a solution of manganous sulphate in strong hydrogen peroxide, then 2—3 drops of 10 per cent. ammonia, heat to boiling,

and filter. A colourless filtrate is obtained, which, if acid dyes be present, assumes a red colour on addition of hydrochloric acid. Basic coal-tar colours give at once a coloured filtrate. If too much wine is employed the filtrate will not be quite colourless.

The author, however, prefers the following process:—To 15 c.c. of the wine add sufficient barium peroxide, then pass carbonic anhydride until the mixture assumes a chocolate colour, but not longer. It will then give a perfectly colourless filtrate, which, on addition of hydrochloric acid, will exhibit characteristic colours if acid dyes are present.

M. J. S.

Reactions for Discriminating between Chrysophanic Acid and the Santonin Colouring Matter in Urine. By G. Hoppe-Seyler (*Chem. Centr.*, 1886, 746).—Aqueous soda produces a red colour in urine containing both the santonin colouring matter and chrysophanic acid. In the former case, the red colouring matter is easily soluble in amyl alcohol, and gradually changes to yellow in contact with atmospheric oxygen, whilst in the latter case the red colouring matter is insoluble or almost insoluble in amyl alcohol, and persists for a very long time. These colours differ also in spectroscopic properties.

J. P. L.

Quantitative Reactions for the Separation of Some Resins. By M. v. Schmidt and F. Erban (*Monatsh. Chem.*, **7**, 655—672).—The authors have applied the methods of Köttstorfer (*Zeit. anal. Chem.*, **18**, 199) and of v. Hübl (*Dingl. polyt. J.*, **253**, 281) for the detection of fats, to the examination of resins, and are enabled to determine the relative amounts of the various resins in a mixture without actual separation. The resins are identified by (1) the amount of potash required to saturate 1 gram of the resin dissolved in alcohol; (2) the amount of caustic potash which combines with 1 gram of the resin when the latter is boiled with an excess of alcoholic potash solution; (3) the percentage of iodine which the resin is capable of taking up. The methods for determining these data are given, and also a table in which are the numbers already determined for the various resins.

In the examination of solutions of resins in alcohol or in turpentine, the liquid is first steam distilled until the distillate shows no acid reaction. The residue is dried at 110°. A systematic method of fractional separation of the resins by means of solvents is described in detail. Tables are also given showing the solubility of resins.

N. H. M.

Test for Tannin. By J. E. Saul (*Pharm. J. Trans.* [3], **17**, 387).—The substance is mixed with water, a few drops of an alcoholic solution of thymol are added, and then concentrated sulphuric acid. Commercial tannin yields a rose-coloured turbid solution, pyrogallol a dull-violet solution, whilst gallic acid remains colourless, or nearly so.

D. A. L.

Separation of Globulin from Albumin in Urine. By A. Ott (*Chem. Centr.*, 1886, 540).—The author points out that the separation of globulin from albumin in urine by saturation with magnesium sul-

phate, is only complete in those cases where at least one-half of the phosphoric acid is in the form of neutral phosphate, otherwise the urine should be brought to this condition by the addition of alkali. 60 grams of magnesium sulphate is added to 50 c.c. of urine, and the solution allowed to remain 24 hours at 30—35°, being shaken occasionally. When these precautions are observed, the results are trustworthy. C. F. C.

Detection of Traces of Albumin. By R. Palm (*Zeit. anal. Chem.*, **26**, 35—38).—The sensitiveness of the test for albumin depending on its precipitation by an acid, can be much increased by dissolving the acid in alcohol, or, better, alcohol containing 10 per cent. of ether; an excess of the reagent will not then redissolve the precipitate.

Sodium sulphantimonate added to an albumin solution made alkaline with ammonia, gives a yellow precipitate. Sodium nitroprusside acidified with acetic acid, and also potassium antimonate, are sensitive reagents, but all three give precipitates with the alkaloïds. The following are free from that defect:—(1.) An alcoholic solution of ferric acetate, previously rendered basic by heating with excess of recently precipitated ferric hydroxide. (2.) An alcoholic solution of basic cupric acetate. The precipitate dissolved in acetic acid and boiled with excess of soda, shows reduction in presence of albumin. (3.) An alcoholic solution of lead acetate or chloride; or (4) a solution of freshly precipitated lead hydroxide in water. This last will detect 1 part of albumin in 500,000 of water. The colourless precipitates from (3) and (4) are adapted for confirmation by Adamkiewicz's test (violet colour on mixing with glacial acetic and sulphuric acids). M. J. S.

Presence of Albumin in Vegetable Tissue: Microchemical Test for Albuminoïds. By F. Krasser (*Monatsh. Chem.*, **7**, 673—697).—The various colour tests for albumin are discussed and shown to be insufficient, as they are also produced by substances other than albuminoïds. When albuminoïds are treated with alloxan an intense purple coloration is produced; the colour is also produced by tyrosine, aspartic acid, and asparagine. The reaction must take place in the cold and the mixture be kept free from ammonia. In testing for albumin, the substance is first washed with hot water to remove other compounds present which give the reaction with alloxan. Millon's reagent (*Compt. rend.*, **28**, 40) is the only one which shows a definite structure in albumin; namely, the presence of a monohydroxylated aromatic nucleus. The reaction has the drawback that it will not take place in the case of a tissue containing much water, owing to the formation of basic mercury salts. In testing for albumin by this method in cellular tissue, the absence of vanillin (the only other substance containing a monohydroxylated aromatic ring which has as yet been found to be present) is determined by Wiesner's phloroglucinol reaction; it is still better to wash the section to be tested with warm water.

The author's methods for detecting albumin consist (1) in showing

the presence of the monohydroxylated aromatic nucleus by Millon's reaction; (2) in showing the presence by means of alloxan of the group $—CH_2·CH(NH_2)·COOH$ formed by the decomposition of albumin after exclusion of aspartic acid and other non-albuminoïd substances. N. H. M.

Detection of Blood Stains in Presence of Iron Rust. By E. Dannenberg (*Chem. Centr.*, 1886, 840—842).—The test for blood based on the formation of hæmin crystals fails when the stain is on rusty iron, in consequence of the insolubility of the compound of hæmin with ferric oxide. The following treatment, however, yields crystals which it would appear are absolutely characteristic of blood. A few drops of strong potash solution is placed on the stain, and the object is—when possible—warmed by a spirit-lamp flame. Meanwhile the stain is loosened by scraping, and the turbid liquid is transferred to a porcelain basin. There it is washed by decantation, pouring away the pale-red ferric oxide, but retaining any heavy, dark-brown, granular substance. This, after draining off the water, is treated with a drop or two of ammonium sulphide and triturated while gently warming. The solution is filtered from the ferrous sulphide, and is examined by Erdmann's method (Otto, *Ausmittelung der Gifte*, 6th Ed., p. 228). The dry residue on the microscope slide is treated with acetic acid—not adding so much as to escape beyond the cover-glass; the acid is then slowly heated just to incipient boiling. On examining with a magnifying power of 300—800 the presence of blood will be indicated by the appearance of elongated, rhombic plates of brown colour, but with a colourless stripe in the direction of the longer diameter. They are found usually at the edges of the drop or of the cover-glass. It appears to be difficult to produce them at will from blood alone, but in 30 experiments with the iron compound no failure occurred. The name *hæmidin* is proposed for these crystals. M. J. S.

Dannenberg's Hæmidin Crystals. By C. Amthor (*Chem. Zeit.*, **10**, 1479).—These crystals, obtained by Dannenberg (preceding Abstract) by treating blood mixed with ferric oxide with ammonium sulphide and water, are now shown to be simply sulphur crystals. D. A. L.

Analysis of Hoofs and Horns. By J. Hughes (*Chem. News*, **54**, 314—315).—The author draws attention to the importance of taking moisture into consideration when analysing hoofs and horns, as, when powdered for analysis, these substances become very hygroscopic. When determining nitrogen in such highly nitrogenous substances by the soda-lime method, the quantity of soda-lime should exceed that generally used in nitrogen combustions; it is doubtful even then if all the nitrogen is obtained as ammonia. D. A. L.

General and Physical Chemistry.

Red Fluorescence of Alumina. By L. de Boisbaudran (*Compt. rend.*, **104**, 330—334).—The author has obtained the red fluorescence with pure alumina after it has been strongly heated.

Alumina which has been heated at a temperature between the melting points of copper and silver gives only a trace of the red fluorescence in a vacuum, but after addition of 0·01 per cent. of chromic oxide, the fluorescence becomes much more intense. The fluorescence increases in intensity with an increase in the proportion of chromic oxide, and is very brilliant when the amount of the latter reaches 0·33 per cent. The spectrum of the fluorescence shows a nebulous band in the region of the line C.

Alumina containing about 6 per cent. of potassium oxide, after it has been moderately heated and mixed with 0·00021 per cent. of manganous oxide, shows no red fluorescence, but a feeble green fluorescence is visible, and this increases in intensity with the proportion of manganese, and becomes very brilliant when the amount of manganese oxide is 1·0, 0·1, or 0·033 per cent. If the mixture is very strongly heated, the green fluorescence becomes much more intense and is very brilliant—even when the proportion of manganous oxide is only 0·001 per cent.

Magnesium oxide, prepared from magnesium sulphate, when mixed with 0·1 per cent. of chromic oxide, shows a brilliant red fluorescence; this is still distinct, although not so intense, with somewhat less than 0·01 per cent. of chromic oxide. The spectrum shows a nebulous band in the region of the line C. If the magnesium oxide is very strongly heated, the fluorescence becomes more intense.

Gallium oxide, prepared from the nitrate and strongly heated, shows a violet-blue fluorescence which changes to a magnificent red when 0·67 per cent. of chromic oxide is added. The red fluorescence is obtained with 0·1 per cent. of chromic oxide, and if the amount of the latter is only 0·01 per cent., the fluorescence is at first blue, but soon changes to red. C. H. B.

Phosphorescence of Alumina. By E. Becquerel (*Compt. rend.*, **104**, 334—335).—Some strongly ignited alumina, obtained from Boisbaudran, showed only a faint, greenish fluorescence in a vacuum, but it showed a bright red phosphorescence in the phosphoroscope when subjected to the influence of the electric arc. The rays in sunlight, &c., which excite the phosphorescence of alumina are between D and F, and from half-way between F and G to H. In a vacuum, the exciting rays are chiefly of much higher refrangibility. The results obtained by different methods of excitation are evidently very different.

If the vacuum in a tube containing rubies is imperfect, the rubies show scarcely any trace of luminosity under the influence of the elec-

tric discharge, but when the exhaustion becomes great, a brilliant red phosphorescence is observed.

It is possible that chromic oxide confers on alumina the power of absorbing different exciting rays, and thus increases its power of phosphorescence. This action would be similar to that exerted by certain dyes on photographic plates. C. H. B.

Phosphorescence. By E. Lommel (*Ann. Chem. Phys.* [2], **30**, 473—487).—By a method already described (*ibid.*, **20**, 847) the author has examined the light emitted by a series of 16 phosphorescent substances prepared by Dr. Schuchardt, and by Balmain's paint. The substances were placed in small mica cells, and sunlight or the electric light, filtered through two blue and two violet glasses and a solution of ammonio-cupric sulphate, concentrated on them by means of a lens. The exciting light thus contained only rays from midway between F and G to the ultra-violet. The phosphorescent light was examined spectroscopically both during illumination and subsequently. The calibration of the spectroscope is very fully described.

None of the specimens were chemically examined. Twelve of them were styled calcium sulphide, one strontium sulphide, and the remaining three double sulphides of strontium and antimony. The calcium preparations emitted light of all colours—from red to violet. The spectra obtained from them were sometimes continuous, sometimes not; but *collectively* they agreed in showing three well-marked and fixed maxima of luminous intensity; namely, I, for $\lambda = 0{\cdot}584$ in the yellow; II, for $\lambda = 0{\cdot}517$ in the green; and III, for $\lambda = 0{\cdot}462$ in the blue. In individual specimens, however, sometimes one, sometimes two of these maxima were either faint or wanting; this giving rise to the various colours emitted by them. The 12 specimens may be divided into five groups according to the maxima present.

Azure-blue and bluish-violet (two specimens), three maxima present.

Blue (2 and Balmain's paint), II and III present.

Violet to rose-red (5), I and III present.

Greenish-blue (1), only II present.

Orange (1), only I present.

After illumination has ceased, some of these maxima may fade more rapidly than others, and hence the tint of the phosphorescence may change.

The spectra of the strontium sulphide (green) and of the strontium antimony sulphides (yellow) were continuous from red to violet; but each showed only one maximum of intensity. During illumination, this maximum was not only differently placed in each case ($\lambda = 0{\cdot}542$ in the green for strontium sulphide : $\lambda = 0{\cdot}556$ in the yellow-green, and $0{\cdot}578$ in the yellow for strontium antimony sulphide), but on withdrawal of the light it appeared to move slightly towards the violet, while the spectrum rapidly faded from the two ends towards the centre.

By inserting a little screen coated with the phosphorescent substance into the eye-piece of the spectroscope, the author has also been able to examine the effect of the various rays of the spectrum on the above substances after they had been excited by a short exposure to daylight.

In every case there was a period of intensified phosphorescence in the parts exposed to the red and ultra-red rays, followed by more or less rapid extinction. As a rule, the first period was very short; but in those specimens in which the green maximum, II, was well developed, the intensifying effect lasted for a long time—sometimes for hours, and even after the red illumination was withdrawn. All calcium preparations showed, in the intensified parts, the luminous bands already described (*loc. cit.*) during illumination; and after the intensifying rays were cut off a dark image of the less refrangible spectrum on a bright background appeared on the screen sooner or later.

By means of the phosphorescent eye-piece, the author has also traced the rays which are most effective in exciting phosphorescence in each case. The general result arrived at is, that the least refrangible rays of the light emitted by the calcium preparations are produced by the most refrangible rays of the exciting light. The same rule holds, though less generally, for the strontium antimony preparations.

CH. B.

Comparative Actions of Heat and Solar Radiation. By E. DUCLAUX (*Compt. rend.*, **104**, 294—297).—A large number of organic compounds containing carbon, hydrogen, and oxygen were subjected to the action of heat or solar radiation in presence of air, silver nitrate, potassium permanganate, platinic chloride, auric chloride, and other oxidising agents.

The results show that all reactions of the nature of combustion which can be produced by the action of heat can also be produced by solar radiation; but several decompositions which are effected by sunlight cannot be brought about by the influence of heat alone. All the decompositions consist in the splitting up of the original molecule into simpler molecules, amongst which may be mentioned formic, acetic, and butyric acids, methyl and ethyl alcohols, and ether—compounds which are relatively stable in the conditions under which they are formed. As a rule, the same substance yields the same products, whatever the nature of the oxidising agent with which it is in contact; but to this law there are a few exceptions. Lactic acid, for example, yields acetic acid when oxidised by the action of air, but butyric acid when oxidised by mercury salts. The stable products of combustion do not exist ready formed in the original molecules, but are the result of a rearrangement of the atoms. This is shown by the fact that the same products are obtained from different substances, and also by the fact that one and the same substance may yield different products under different conditions. As a rule, the products contain a smaller number of hydrogen and carbon-atoms than the original substances, the exceptions being formic acid, which is obtained from oxalic acid, and butyric acid which is obtained from lactic acid. Potassium permanganate, which in many cases will act in the dark, yields the same products as the action of sunlight, and the compounds, which it attacks most readily, are those which are also least stable in contact with other oxidising agents. It constitutes the most convenient reagent for determining the influence of alkalinity, acidity, &c., on the rate and limit of the oxidising action.

C. H. B.

Simple Form of Water Battery. By H. A. Rowland (*Amer. J. Sci.*, **33**, 147).—Strips of zinc and copper, each 2 inches wide, are soldered together so as to make a combined strip rather less than 4 inches wide. This is then cut into pieces about a quarter of an inch wide, each composed of half zinc and half copper. A thick plate of glass, a foot square, is heated and coated with shellac, and to this are stuck the strips of copper and zinc which have been bent into the shape of the letter U, with the branches a quarter of an inch apart. The soldered portion is fixed in the shellac, and the two branches stand up in the air, so that the zinc of one piece comes within one-sixteenth of an inch of the copper of the next one. A row 10 inches long will thus contain 30 elements. The rows being placed one-eighth of an inch apart, a space 10 inches square will contain 800 elements. The plate is carefully warmed, and a mixture of beeswax and resin is poured on to a depth of half an inch. The back of the plate is fitted into a wooden frame with a ring screwed in the centre, so that the whole can be suspended with the elements below. When required for use, the tips of the elements are dipped into a pan of water, and the battery again hung up. The space between the elements will hold a drop of water that will not evaporate for an hour. The battery is thus in operation in a minute, and is perfectly insulated by the glass and cement. B. H. B.

Sodium Dichromate Cell. By S. L. Harding (*Amer. J. Sci.*, **33**, 61—66).—The author has made a series of comparative tests of sodium dichromate and potassium dichromate with reference to the relative constancy or powers of endurance, the electromotive force, and the resistance of the two batteries. The cells, in every case, were set up like the Bunsen battery; the proportions used being those given by the chemical reactions which take place within the cells.

Resistance.—Lodge's method was used for determining the resistance of the cells. For the sodium dichromate cell the resistance was found to be 0·4967 ohm, and for the potassium salt cell it was 0·468 ohm. The resistances of both cells could undoubtedly be reduced if occasion should demand it.

Electromotive Force.—The electromotive force of the sodium salt cell, obtained by the open circuit method of comparison, was 1·893 volts. That of the potassium salt cell was found to be 1·852 volts. The electromotive force of the ordinary Daniell cell was 1·059 volts.

Constancy.—The author obtained a series of photographic records of cells set up with the two dichromates, by substituting a sheet of sensitive paper for the ground glass scale of the reflecting galvanometer (see *Amer. J. Sci.*, **29**, 374). The sodium salt cells, it was found, ran on an average fully 20 hours, or more than one-third longer, than the potassium salt cells. The greater power of sodium dichromate is due to the fact that, of the two dichromates, the sodium salt can provide the greater amount of oxygen to unite with the hydrogen set free at the negative electrode. The chemical reactions for the two salts are exactly similar; the oxygen coming from the chromic

acid in both cases. The salt which, for a given weight of the solution, can furnish the most chromic acid is the superior. The solubilities of the two salts are as follows:—At 15°, 100 parts of water dissolve 12·5 parts of potassium dichromate and 83·16 parts of anhydrous sodium dichromate. The available oxygen, therefore, in a saturated solution is 0·0852 per cent. for the sodium salt, as compared with 0·0180 per cent. for the potassium salt. B. H. B.

Ferric Chloride as an Exciting Agent for Voltaic Batteries. By H. N. Warren (*Chem. News*, **55**, 49).—The power of a current from an ordinary dichromate cell may be very greatly increased by employing a slightly acidified, strong solution of ferric chloride mixed with bromine, in place of the potassium dichromate. The bromine serves to reoxidise the ferrous chloride formed, and when consumed may be again set free by the addition of bleaching powder. D. A. L.

Specific Inductive Power of Liquids. By Negreano (*Compt. rend.*, **104**, 423—425).—The author has determined the dielectric constants K and the refractive indices of benzene (both pure and mixed with thiophen), toluene, xylene (mixture of isomerides), meta-xylene, pseudocumene, cymene, and terebenthene. The square roots of the dielectric constants differ from the refractive indices in the second decimal place only. The dielectric constant seems to decrease with a rise of temperature within certain limits. In the series examined, the value of the dielectric constant increases as the molecule becomes more complicated. The ratios $\frac{\sqrt{K}-1}{d}$ and $\frac{K-1}{d}$ increase irregularly with an increase in molecular weight. The ratio $\frac{K-1}{(K+2)d}$, however, is practically constant, and for the same liquid is the relation which connects the dielectric constant with the density. In this particular series, the value of this constant is about 0·34.

	T.	K.	$\sqrt{K}$.	Refractive index, n_D.	Density.	$\frac{K-1}{(K+2)d}$.
Benzene, with thiophen	26°	2·3206	1·5316	1·4974	0·8803	0·34
„ another sample	25	2·2988	1·5172	1·4978	0·8756	0·34
„ pure	14	2·2921	1·5139	1·5062	0·8853	0·34
Toluene	27	2·242	1·4949	1·4912	0·8608	0·34
„	14	2·3013	1·5165	1·4984	0·8711	0·346
Xylene	27	2·2679	1·5059	1·4897	0·8554	0·345
Metaxylene	12	2·3781	1·5421	1·4977	0·8072	0·36
Pseudocumene	14	2·4310	1·5591	1·4837	0·857	0·37
Cymene	19	2·4706	1·5716	1·4837	0·851	0·38
Terebenthene	20	2·2618	1·5039	1·4726	0·875	0·337

C. H. B.

Electromotive Force of some Thermo-elements consisting of Metals and Solutions of their Salts. By A. Ebeling (*Ann. Phys. Chem.* [2], **30**, 530—543).—According to Gore (*Proc. Roy. Soc.* **36**, 50, and **37**, 251), the electromotive force of a thermo-couple formed of a metal and a salt solution changes with the concentration of the solution; according to Bouty (Abstr., 1881, 336), who employed the same metal in the electrodes and the solution, it is independent of the concentration. The author has, therefore, reinvestigated the question, using pure copper in contact with copper sulphate or nitrate, and amalgamated zinc free from arsenic in contact with zinc sulphate, nitrate, or chloride. An element consisted of two glass cylinders containing the air-free solution, and communicating through a narrow glass syphon tube. In each mass of liquid was immersed an accurately graduated thermometer, round the bulb of which the metal was wound in the form of wire. One cylinder was surrounded by melting ice, and the other heated to various temperatures. The electromotive force was measured by Du Bois Raymond's modification of Poggendorff's compensation method, using two Daniell cells which were from time to time compared with Helmholtz's constant calomel cell.

It was impossible to find two wires of the same metal so perfectly homogeneous as to give no current in the above cell, even with both contacts at the same temperature. The strength of this chemical current was therefore measured at constant temperature before and after each set of experiments, the rate of its change with time calculated, and a correction thus made. Since observations with different elements could not all be made at precisely the same temperature, this source of error was allowed for on the assumption that the electromotive force is proportional to the difference in temperature of the contacts. The temperature intervals were 20°, 35°, and 47°. Tabular statements of the results in each case are given. The author's conclusions are:—

The electromotive force is not proportional to the difference of temperature of the contacts, but increases with it in some greater ratio.

With any constant temperature difference, the electromotive force diminishes slightly with the time, probably as the result of chemical actions.

The electromotive force does not increase continuously with the concentration, but exhibits maxima and minima.

For the same acid, these maxima correspond with the same state of concentration.

Some idea of the results may be gathered from the following table of electromotive forces due to a difference of temperature = 20°. P signifies the percentage of anhydrous salt in solution.

The results are expressed in terms of a calomel cell as unit. To reduce them to electromagnetic units the figures must be multiplied by $10542 \cdot 10^4$ cm.$^{\frac{3}{2}}$g.$^{\frac{1}{2}}$sec.$^{-2}$. The maxima for strong solutions are indicated by brackets, for weak solutions by asterisks.

Certain other conclusions are also stated, but with some reserve. According to Neumann's law, substances of similar constitution and

P.	Cu – $CuSO_4$.	Zn(α) – $ZnSO_4$.	Cu – $Cu(NO_3)_2$.	Zn(α) – $Zn(NO_3)_2$.	Zn(α) – $ZnCl_2$.
69	—	—	—	—	0·00368
60	—	—	—	—	0·00813
55	—	—	—	—	0·01001
50	—	—	—	—	0·01066
45	—	—	—	—	0·01086
40	—	—	—	—	0·01064
35	—	—	0·01094	0·01474	0·01045
30	—	0·01466	0·01163	0·01710	0·01018
25	—	0·01484	0·01219	0·02027	0·00995
20	0·01530	0·01517	0·01209	0·01629	0·00971
15	0·01360	0·01514	0·01109	0·01732	0·00951
10	0·01100	0·01495	0·01137	0·02438	0·01029
5	—*	0·01465	0·01130*	0·02238*	0·01129*

properties have equal atomic heats; but according to the fourth statement above the maximum electromotive force for different metals, but the same acid, occurs for solutions of different concentration. Also, the strength of solution for which the electrical conductivity is a maximum is also that for which the electromotive force is a maximum. This is shown by a table of electrical conductivities taken from Wiedemann's *Electricity*. Finally it appears that here, as in the case of ordinary thermo-couples, the worst conductors make the most effective combinations. CH. B.

Galvanic Polarisation of Aluminium. By F. STREINZ (*Phil. Mag.*, [5], **23**, 304).—The author finds that if aluminium plates be polarised, the difference of potential between the oxygen plate and the zinc of the polarising cell increases within very wide limits with the electromotive force of the cell, whilst the hydrogen plate shows very little polarisation for small electromotive forces, but with large electromotive forces acquires a difference of potential opposite in direction to that usually obtained. The small amount of gases usually obtained from aluminium electrodes can be explained by the great opposing force of oxygen polarisation. H. K. T.

Conductivity of Mixtures of Aqueous Solutions of Acids. By S. ARRHENIUS (*Ann. Phys. Chem.* [2], **30**, 51—76).—Previous observations by Bouchotte, Paalzow, Bender, and Klein, have led to no general conclusions. In the following experiments, the author has used Kohlrausch's method, employing a telephone as indicator.

The fact that the molecular conductivity of a solution is not proportional to the amount of dissolved electrolyte, proves that the solvent liquid is not always uniformly distributed amongst the dissolved molecules, even when the electrolyte is a single substance. Ostwald, however, by some experiments, which are here described for the first time, has shown that the molecular conductivity of a mixture of butyric and acetic acid solutions in any proportions, is always the sum of the molecular conductivities of the constituent solutions.

Each electrolyte behaves as if the other were absent. Such solutions are termed by the author "isohydric."

In the foregoing case, the two acids are very similar; but when they are of different character, their solutions can be isohydric only under special conditions. Now, the specific conductivity of any solution is directly proportional to the contained mass of electrolyte, and inversely proportional to the frictional resistance to the transference of the ions. For dilute solutions, the latter may be regarded as not changing with dilution. Hence, when two weak solutions are mixed, and the distribution of the water is not thereby altered, the conductivity is the arithmetical mean of the separate conductivities; or if l_1v_1 and l_2v_2 are the specific conductivities and volumes of the original solutions, and L and $(v_1 + v_2)$ those of the mixture—

$$(\mathrm{L}v_1 + v_2) = l_1v_1 + l_2v_2 = \mathrm{N}_1\mu_1 + \mathrm{N}_2\mu_2,$$

where N_1 and N_2 are the numbers of dissolved gram-molecules, and μ_1, μ_2 the molecular conductivities of the electrolytes.

When the distribution of the water is altered by mixture, let v_1 and v_2 become $v_1 + d\mathrm{V}$ and $v_2 - d\mathrm{V}$; then L_1, μ_1, and μ_2 will increase by $d\mathrm{L}_1$, $d\mu_1$, and $d\mu_2$. Therefore—

$$(v_1 + v_2)d\mathrm{L} = \left(\mathrm{N}_1\mu_1\frac{d\mu_1}{\mu_1 d\mathrm{V}} - \mathrm{N}_2\mu_2\frac{d\mu_2}{\mu_2 d\mathrm{V}}\right)d\mathrm{V}.$$

The ratios $d\mu_1/\mu_1 d\mathrm{V}$ and $d\mu_2/\mu_2 d\mathrm{V}$ can be calculated from Ostwald's data (*J. pr. Chem.* [2], **32**, 300). For a small increase of v_1, $d\mu/\mu d\mathrm{V} = \sigma$, where the values of σ are different for different acids, and also diminish gradually with dilution. Finally, $(v_1 + v_2)d\mathrm{L} = (l_1\sigma_1 - l_2\sigma_2)d\mathrm{V}$.

The author has calculated σ for solutions of equal conductivity of six different acids, and finds that its value is greater the more feeble the acid (strength = molecular conductivity). When, therefore, two solutions of different acids, of not very different conductivity, are mixed, and when the specific conductivity of the mixture is found to be greater than the arithmetical mean of the specific conductivities of the original solutions, then the more feeble acid has taken part of the solvent water from the stronger; and *vice versâ*. When the conductivity of the mixture is equal to the above arithmetical mean, the solutions are isohydric.

In practice, it is desirable to compare feeble acids with a stronger acid, rather than with each other, so that σ_1 and σ_2 may be as different as possible; and to use equal volumes, since $d\mathrm{V}$ is then a maximum. The solutions should also be dilute, and of such strengths that their specific conductivities do not greatly differ. From two observations, then, in which one solution is varied, the isohydric strengths can be found by linear interpolation.

The following propositions are experimentally proved. If two solutions are isohydric when mixed in equal volumes, they are also isohydric when mixed in any other ratio. If a solution A is isohydric with solutions B and C, B and C are also mutually isohydric.

Mutually Isohydric Acid Solutions.

Hydrochloric.	Oxalic.	Phosphoric.	Tartaric.	Formic.	Acetic.
0·1737	0·513	—	—	—	—
608·9	607·3	—	—	—	—
0·04611	0·06255	0·337	—	—	—
168·8	139·7	225·6	—	—	—
0·0238	0·0331	0·0764	0·52	—	—
88·59	85·07	82·2	75·0	—	—
0·00475	0·00488	0·00702	0·026	0·1077	1·00
17·98	16·27	16·11	16·41	16·85	13·81
0·001402	0·00135	0·00163	0·00324	0·01261	0·0965
5·396	4·915	4·926	4·903	5·467	4·885
0·000349	0·000396	0·00044	0·000498	—	0·009175
1·524	1·582	1·479	1·499	—	1·476

In this table, isohydric solutions are arranged in *horizontal* series. The upper of each pair of numbers gives the corresponding strength of the solution in gram-molecules per litre; the lower gives the conductivity in mercury-units $\times 10^8$. The latter is uncertain, sometimes to the extent of 5 per cent.

From the table, it may be seen that the conductivities of isohydric solutions are usually about equal. It is also shown that solutions of equal conductivity are approximately isohydric. The difference in the latter case is usually a slight *increase* of conductivity.

By a method of approximations, the conductivity of any mixture of these acids may be calculated from Ostwald's data. No simple relation exists between the molecular strengths of isohydric solutions, such as Bender (*Ann. Phys. Chem.* [2], **22**, 197) claims to have proved.

Ch. B.

Theory of Voltaic Action. By J. Brown (*Proc. Roy. Soc.*, **41**, 294—315).—A number of experiments are described in this paper to establish the two following propositions: (1) that the difference of potential near two metals in contact, as observed by Volta's bimetallic condenser method or Thomson's quadrant method, is due to the chemical action of a film of condensed vapour or gas on the surfaces of the metals; (2) that these two metals, with their liquid film, form a cell similar to one composed of the same metals as elements, and a liquid of the same kind as electrolyte, which in contact experiments is divided by the intervening insulating diaphragm of air or other gas. From this it follows that in these experiments it is the difference of potential at the outer surfaces of the two metals which is measured. Thus, in the case of a single metal covered by its chemically active electrolytic film, at the surface of the film and metal there is an electromotive force corresponding with the chemical action between

them. In the case of two metals joined metallically, the potentials of the metals will be equalised, a portion of the negative charge going through the connection between the two metals, and thence to the film.

In the experiments, a pair of metals were taken, each of which was carefully cleaned, and the difference of their potential determined immediately; into the apparatus, a gas which acts chemically on the metals was then introduced, and the difference of potential determined after various intervals of time. The gas causes an immediate reversal of the potential; this is compared with a similar reversal which occurs when a solution of the same gas is added to water in which the same pair of metals is immersed. Experiments were made with copper-iron in ammonia and hydrogen sulphide, silver-iron in hydrogen sulphide, and copper-nickel in ammonia and hydrochloric acid gases, and the results compared with those obtained by adding solution of ammonia, hydrochloric acid, and potassium sulphide to water, in which these several pairs of metals were immersed. It would appear from these results that no contact experiment with clean metals has as yet been made, since they are cleaned whilst exposed to the atmosphere, and are thereby covered with a film of condensed water containing dissolved gases. Experiments are quoted to show that the difference of potential of a copper-zinc pair in air is reduced by the introduction of dehydrating agents, such as sodium and phosphoric anhydride. It was further found possible to join the films only on the two metals, without bringing the metals themselves in contact, and thus to produce an electromotive force from metals apparently dry; the thickness of the environing film was determined by means of a micrometer screw.

From the above experiments, it follows that difference of potential in a pair of metals is not an intrinsic property of the metals in themselves, but results from a chemical action induced by their exposure to the atmosphere; this action proceeds until terminated by its own effects.

Thus, in the case of a copper-zinc pair in air, the oxygen of the moisture combines with the zinc, and thus is produced a configuration of oppositely electrified atoms, forming a double layer. This idea has been put forward by Helmholtz in illustration of the phenomena of electrolysis, and successfully applied to explain polarisation.

V. H. V.

Electric Accumulators. By D. Drake and J. M. Graham (*Dingl. polyt. J.*, **262**, 382).—From the results of a series of experiments on the permanency of accumulators, the authors draw the following conclusions:—(1.) The duration of lead plates or conductors and the retention of their structure is not dependent on the amount of current condensed in and discharged from the cells. (2.) New cells or cells which have been out of use for some time should be charged to the maximum extent. (3.) The cells should not be completely exhausted; moreover, it is proposed not to discharge them beyond the point at which the E.M.F. begins to be sensibly reduced. (4.) The film of dioxide formed during the condensation of the current is said to protect the plate from the injurious effects of overcharging and

local action. (5.) A certain (small) amount of sulphate is necessary to hold the active material together; an excess, however, causes the oxide to separate from the conductor. D. B.

Determination of Atomic Weight from Specific Heat. By G. Janeček (*Chem. Centr.*, 1887, 3—4).—The author denies, on theoretical and experimental grounds, the correctness of the law of Dulong and Petit. Of the 70 known elements, there are only 16 whose atomic heats can be shown to undoubtedly lie between 6·028 and 6·849, whilst there are two (S and P) much below 6, one (Si) between 4 and 5, one (Be) about 3·8, one (B) about 2·5, one (C) about 2, and five (Al, Cr, Cu, Fe, and Ga) between 10·4 and 12·6. For all the remaining elements, the atomic weight has simply been adjusted to the law of Dulong and Petit. The atomic heats of the gaseous elements in their solid condition have been deduced almost exclusively from such arbitrary values. Of the values so obtained, only those of two elements (Cl and N) correspond in some degree with the law of Dulong and Petit, whilst those of the others (F, O, and H) do not at all agree. Weber's researches on the influence of temperature on the specific heat of the solid elements afford no support to the law. Weber's numbers for carbon, boron, and silicon do not refer to the absolute specific heat, but rather show the entire absorption of heat under different conditions. It is possible to calculate the atomic heats from the differences in the observed values, and the numbers obtained have been used to confirm the law of Dulong and Petit. The conclusions, however, which are applicable to these three elements may also be applied to all the other elements, the atomic heats of which have been calculated from specific heat determinations made at an arbitrarily selected temperature. When this temperature is departed from for the specific heat determinations, the agreement of the atomic heat with the law of Dulong and Petit entirely disappears. G. H. M.

Specific Heats of Liquids. By M. Langlois (*Compt. rend.*, **104**, 420—422).—The author has defined the terms *enveloping molecule* and *secondary molecule* in a previous communication. His experiments on the heat of vaporisation show that the enveloping molecule, considered by itself, behaves as a true liquid molecule. The secondary molecules, on the other hand, behave like gaseous molecules, and consequently in calculating the specific heat of a liquid, it is merely necessary to calculate the heat which they would absorb in the gaseous state when expanding under constant pressure. The variations in the attraction on the molecular surface are so small within a comparatively narrow range of temperature, that they may be neglected. When the temperature of an enveloping molecule is raised, it experiences an alteration in the force of atomic translation, and this results in an oscillating motion with absorption of a quantity of heat, which the author defines as the *heat of oscillation*. From these considerations, the author has calculated the specific heats of water, carbon bisulphide, chloroform, carbon tetrachloride, ether, ethyl alcohol, and acetone, and has obtained numbers which agree closely with the actual determinations of Regnault. C. H. B.

Isomerism of Position. By A. Colson (*Compt. rend.*, **104**, 428—430).—The author has determined the specific heats and the heats of fusion of the dibromo-, dichloro-, and tetrachloro-xylenes:—

	Sp. heat.		D.	C × D.	
	15—40°.	15—60°.			
Dibromoparaxylene	0·180	0·188	2·012	0·362	15·3
Dibromortho-xylene	0·183	0·190	1·988	0·363	15·4
Dibromometaxylene	0·184	0·191	1·959	0·361	15·2
Dichloroparaxylene	0·282	—	1·417	0·414	—
Dichlorortho-xylene	0·283	—	1·393	0·394	17·0
Dichlorometaxylene	0·295	—	1·370	0·404	16·2
Tetrachloroparaxylene	—	0·242	1·606	0·290	14·7
Tetrachlorortho-xylene	—	0·24	1·601	0·288	14·3
Paraxylene	—	—	—	—	14·4

The last column contains the values obtained by multiplying the molecular weight into the number obtained by dividing the latent heat by the absolute temperature of fusion. The higher values obtained for the bromine-derivatives may be due to their greater instability, or to the fact that the mean specific heat (0·199) used in calculating the numbers is too high. If the results can be generalised, it follows that at the melting points the difference between the entropy of the liquid and solid is constant for all isomerides of position. When the results are calculated to the molecular weights, it is found that this difference will not be sensibly altered by the substitution of chlorine for hydrogen. The heat of fusion L is connected with the temperature t, pressure p, and contraction $v'-v$ by the equation of Clausius and Clapeyron:—

$$\frac{L}{273 + t} = \frac{1}{425}(v' - v)\frac{dp}{dt}.$$

From the author's results, it follows that for isomerides of this kind the first term in this equation is constant, and hence

$$t = K(v' - v)(p - p_0),$$

or the temperature of fusion increases proportionally with the pressure. C. H. B.

Determination of the Constitution of Carbon-compounds from Thermochemical Data. By H. E. Armstrong (*Phil. Mag.* [5], **23**, 73—109).—The author quotes the chief results obtained by Thomsen (*Thermochem. Unters.*, Bd. iv) in the determination of the heats of combustion of a large number of carbon-compounds, and criticises the views there put forward with reference to their constitution. In Thomsen's work, all the heats of combustion are based

on the assumption that the substance burned is in the state of gas at 18°, and that the products are gaseous carbonic anhydride and liquid water at that temperature; before, however, these data can be applied to the determination of the constitution of the compounds themselves, it is necessary to deduce the heat of combustion of gaseous atomic carbon, a value denoted by the symbol $f(C_l)$. The argument by which this value, $f(C_l)$, is estimated by Thomsen is as follows:— The heat of combustion of carbon in its compounds is greater than that of amorphous carbon, and the average value obtained by the comparison of the heats of combustion of compounds differing in constitution by one or more atoms of carbon is 121090 units; these comparisons are instituted between a saturated and an unsaturated compound, the latter being formed from the former by the addition of a carbon-atom, which, it is usually said, becomes doubly linked with another carbon-atom. Now, if carbonic anhydride were capable of combining with an atom of carbon, it is to be supposed that it would form an unsaturated compound $CO : CO$, bearing the same relation to it that ethylene bears to methane, and that the heat of combustion of this compound would exceed that of carbon dioxide by 121090 units; whence it follows that the heat of combustion of carbonic anhydride being *nil*, the heat of combustion of the product in question should be 121090 units. But in point of fact, 2 mols. of carbonic oxide are produced by assimilating an atom of carbon with a molecule of carbonic anhydride, the double linkage being annulled whilst the volume is doubled. In the act of expansion 580 units are absorbed; hence the heat of combustion of the product of the union of an atom of carbon with a molecule of carbonic anhydride exceeds 121090 units by the amount absorbed in the separation of doubly-linked carbon-atoms (v_2), plus 580 units, or $f(C_l) = 121090 + v_2 = 135920 - 580 = 135340$ units; whence also $v_2 = 14250$ units.

Very important conclusions are drawn by Thomsen with reference to the heat developed in the combinaton of carbon-atoms by *one*, *two*, or *three* affinities of each, that is, in the way in which they are assumed to be associated in the paraffins, in ethylene, and in acetylene respectively—these values are severally denoted by v_1, v_2, and v_3. These values can be deduced from the heat of formation of compounds containing carbon-atoms united by one, two, or three affinities, as the case may be, by employing as a constant the heat developed by the union of 1 gram-molecule of hydrogen with gaseous atomic carbon. This constant ($2r$) is evaluated thus: the heat of formation of methane, CH_4, at constant volume, calculated on the assumption that it results from the combination of *ordinary* hydrogen with gaseous atomic carbon—of 2 hydrogen *molecules* with 1 carbon-*atom*—is 59550 units; halving this number, $2r$ is found to be 29775 units. With regard to the value of v_1, the heat developed in the formation of ethane, C_2H_6 (104160 units), results from the combination of 3 hydrogen molecules with 2 carbon-atoms, and of these carbon-atoms with each other by single affinities; hence, $(2C,3H_2) = 3.2r + v_1 = 104160$ units $\therefore v_1 = 14835$ units. The value of v_2 has already been determined to be 14250 units, whilst that of v_3 can be obtained from the heats of

formation of acetylene (28990 units), allylene (74610 units), and dipropargyl (133080 units), and is found to be −81 units, a value so small that it can be neglected. From these values, it follows that the same amount of heat is developed in the combination of carbon-atoms, whether they become singly or doubly linked—in other words, there is no difference between these modes of union—whilst the so-called treble linking of carbon-atoms is unattended with the development of heat.

In addition to his already published views on the constitution of benzene (Abstr., 1881, 89), pyridine, and thiophen (Abstr., 1885, 1126), the following are among the more curious conclusions having reference to the constitution of carbon-compounds arrived at by Thomsen by the use of these values of v_1, v_2, and v_3: phenol is ranked with primary alcohols; ethylene oxide is in reality methylene oxide, $CH_2{\cdot}O{\cdot}CH_2$; aldehydes are unsaturated substances of the general formula $R{\cdot}C(OH)$; methylal and methyl orthoformate contain hydroxyl and are analogous to alcohols in constitution; cyanogen has the formula $N : C : C : N$, and the amines are compounds of pentad nitrogen; methylamine, for example, is $H_2C : NH_3$, dimethylamine, $H_2C : NH_2Me$, and trimethylamine, $H_2C : NHMe_2$, although aniline is found to be $Ph{\cdot}NH_2$; the nitro-paraffins are nitroso-alcohols, nitro-methane being formulated $CH_2{\cdot}(NO){\cdot}OH$; and finally pyridine is not analogous in constitution to benzene.

The author recalling some of these results, and noting the conclusion that $v_1 = v_2$—in other words that there are no such things as double bonds—and that $v_3 = 0$, namely, that in acetylene there is not even a single bond between the carbon-atoms, adds that it cannot be admitted by chemists that ethylene oxide is methylene oxide, whilst Thomsen's formulæ for the amines are altogether improbable. The method of proof that the carbon-atoms are united in ethylene oxide and that the amines have the constitution usually assigned to them, is the method by which the constitution of compounds generally is arrived at, and results obtained by this method would have to be retained in some instances but rejected in others were Thomsen's views adopted. The explanation of these anomalous results is most probably to be found in the view that the true heat of combustion of gaseous atomic carbon is greater than 135340 units. Thomsen's determination of this value involves the assumption that the addition of the first and second atom of oxygen to a carbon-atom involves the development of the same amount of heat, but consideration of the properties of carbonic oxide (such as its tendency to combine with but a limited number of other substances, and, as a rule, only under special conditions) appears to favour the contrary view that, of the total heat developed in the formation of carbonic anhydride, the larger proportion is evolved in the combination of the carbon-atom with a single oxygen-atom—in other words, $f(C_1) = 135340 + x$, where x has probably a high value.

Among the results independent of the value of $f(C_1)$, Thomsen finds that in the formation of haloïd derivatives of hydrocarbons, the addition of a *single* atom of chlorine to methane, for example, is attended with a heat-evolution of only 13500 units; that of *two*,

2.16500 units; that of *three*, 13500 + 2.16500 units; and that of *four*, 2.13500 + 2.16500 units. Again, among the alcohols, the primary are found to have the highest, and the isomeric tertiary the lowest heats of combustion, the secondary occupying an intermediate position. These results are attributed by the author to the effect of the local accumulation of negative elements in the molecule.

W. P. W.

Note on the Foregoing Communication. By S. U. Pickering (*Phil. Mag.* [5], **23**, 109—112).—The author points out that if Thomsen's value of $f(C_1)$ be erroneous, the only meaning then attaching to his values of v_1, v_2, and v_3 will be that they are the *differences* between their actual values. Adopting Armstrong's view that $f(C_1) = 135340 + x$, it is shown that the value for r will become $r + \frac{x}{4}$, while those of v_1, v_2, and v_3 will be converted into $v_1 + \frac{x}{2}$, $v_2 + x$, and $v_3 + \frac{3x}{2}$, respectively. If, as is most probable, x represents some number considerably larger than 14000 units, the heat developed in the union of two carbon-atoms will be very nearly, though not quite, proportional to the number of bonds by which they are united.

Thomsen's argument that the aldehydic radicle consists of hydroxyl rests on the fact that the heat of formation of H·C : O in the aldehydes, together with that of C : O in the ketones, was found to be equal to that of O : C·OH in the acids; the introduction of x, however, destroys this equality, for the sum of the heat of formation of the aldehydic and ketonic radicles will exceed that of carboxyl by $\frac{x}{2}$, and this excess renders the results entirely in accordance with the generally accepted views concerning the constitution of these substances.

W. P. W.

Criticism of Thomsen's Theory of the Heat of Formation of Organic Compounds. By J. W. Brühl (*J. pr. Chem.*, **35**, 181—204, and 209—236).—Starting with the premise that conclusions drawn from experiments undertaken with the object of ascertaining the molecular structure of compounds from physical considerations require, for the present at least, a general confirmation from chemical data, since this question has been studied for a longer time and to a greater degree by chemical than by physical methods, the author submits that such conclusions must be received with caution when they lead to constitutional formulæ which are inexplicable, having regard to the methods of formation and the chemical properties of the compounds concerned. The views on the constitution of carbon-compounds put forward by Thomsen (*Thermochem. Unters.*, Bd. iv) are of this nature (compare preceding Abstracts), and the author criticises these views with the object of demonstrating that they are untrustworthy and based on fallacious arguments.

With regard to the calculation of the fundamental constant v_2

(*loc. cit.*), it is noted that Thomsen assumes without any experimental proof that the union of gaseous atomic carbon with two atoms of oxygen is attended with the development of twice as much heat as when combination ensues with one atom; and further that the value of $v_2 = 14250 \pm 5000$, if the extreme values be substituted for the mean deduced from 14 comparisons of the heats of combustion of saturated and unsaturated compounds. Moreover, the values of the fundamental constants, v_1 and r, and the conclusion $v_1 = v_2$, deduced in the first instance from the heat of formation of hydrocarbons, are assumed by Thomsen to hold for all classes of compounds, and on these values he bases his theories of the constitution of carbon-compounds, although the author shows that assuming v_1 and r constant, v_2 has among others the values 7500 units, 9590 units, and 11110 units (deduced from the heats of formation of allyl and ethyl alcohols, the ethers, and formates respectively).

The method adopted by the author in his criticism is well illustrated in the section of the paper devoted to the consideration of Thomsen's views of the constitution of aldehydes, ketones, acids, and ethereal salts. Thomsen deduces the heat of formation of COH (65400 units), CO (54250 units), and CO·OH (119960 units), by subtracting from the heat of formation of the aldehyde, ketone, or acid the amount of heat assumed to be developed in the formation of the contained hydrocarbon radicle, it being assumed that in these compounds $v_1 = 14200$, and $r = 15000$ units; and since 65400 + 54250 = 119650, he argues that the aldehyde radicle contains hydroxyl, thus C·(OH). No evidence is offered of so surprising a conclusion, and with the same right that Thomsen argues that the group CO in formic, acetic and propionic acids has the same value as CO in acetone, the author submits that the residue, C(OH), of the acids should be supposed to have the same value as it has in methyl, ethyl and propyl alcohols, that is, 44600 units, whence 119650 = 44600 + 75050, and CO = 75050 units. But even if Thomsen's unproved assertion that the heat of formation of the CO-group in the ketones and acids has a constant value = 54250 units be accepted, it does not follow that because in this case the heat of formation of the COH residue must be 65400, a similar value to that already deduced for the aldehyde residue from independent considerations, that the aldehyde radicle must have an analogous constitution any more than a similar sp. gr., boiling point, or other physical property establishes the identity of two compounds. Adopting Thomsen's value that the heat of formation of the aldehyde radicle = 65400 units, and that $r = 15000$, the constitution H·C : O would lead to a value for CO = 50400 units, a value not very different from that of CO in acetone; that the value should be exactly the same even in one and the same series is scarcely to be expected: for example, in the alcohols the heat of formation of C(OH) varies between 41800 and 61600, and in the acids = 65400 units, so that Thomsen's view that the aldehyde radicle contains hydroxyl must be regarded as arbitrary.

Passing on to acetic anhydride, Thomsen calculates for the heat of formation of the group O : C·O·C : O, the value 165940 units, and, inasmuch as 165940 = 3 . 55310, assumes that the heats of

formation of the groups C·O·C and C : O are identical. But as, in the case of the ethers, Thomsen has deduced for the heat of formation of C·O·C the value 31500 units, and since 165940 = 31500 + 2 . 67220, the heat of formation of C : O must be 67220 units instead of 55310; hence the author urges that the fundamental hypothesis of the thermal constancy of the affinity between carbon and oxygen is disproved, inasmuch as the heat of formation of the group C : O or C·O·C is shown to be variable. Moreover, comparing Thomsen's value of the heat of formation of the group C : O in ketones and acids, 54250 units, with the value of this group in carbonic oxide and carbonic anhydride which, according to Thomsen's fundamental assumption, must be 67670 units, the difference between these values, 25 per cent., is irreconcilable with the hypothesis on which the whole theory is based.

With regard to ethereal salts, the author severely criticises the argument by which Thomsen is led to deduce the value 105000 units for the heat of formation of the group O : C·O·C, and to alter the formulæ of those salts in which there is a marked deviation from this average value; moreover, it is pointed out that the formula proposed for ethyl acetate, OH·CHMe·CMe : O, and calculated from the equation $7r + 3v_1 + 54250 + 65400 = 267250$ (the actual value being 265910), is based on an entirely wrong conception, inasmuch as Thomsen's proposed formula for the aldehyde radicle is R·C(OH). This radicle is not present in the proposed formula for ethyl acetate, and as a compound of the formula given would most probably resemble a secondary alcohol, the value of the heat of formation of C(OH) in isopropyl alcohol, namely, 50710 units, ought to be substituted for 65400, giving a total 252560, which in nowise agrees with the experimental results. Criticising in a similar manner Thomsen's views with regard to the molecular structure of the other classes of carbon-compounds, for details of which the paper must be consulted, the author concludes that they cannot be maintained, and finally calls attention to the controversy which has arisen as to the correctness of Thomsen's value for the heat of combustion of benzene.

W. P. W.

Thomsen's Investigations. By F. Stohmann (*J. pr. Chem.* [2], **35**, 136—141; compare Abstr., 1886, 842).—In determining the heat of combustion of liquid ethyl ether the mean 8805 cal. per gram or 651570 per gram-mol. was obtained. Thomsen obtained the number 660200 cal. as the mean of the series of experiments in which the ether was burnt partly as vapour mixed with air, partly in a universal burner as vapour at 22°. Thomsen's number when corrected gives 652830 cal.

A second series of experiments is described in which the ether is burnt as gas at 17° in a current of oxygen by the method employed for burning benzene vapour (*J. pr. Chem.* [2], **33**, 256). The mean number 8921 cal. per gram, equal to 660175 cal. per gram-mol., was obtained. Thomsen found the heat of combustion of ether at 18° to be 659600 cal. These experiments show that the author and Thomsen obtain concordant results when working under the same conditions.

The author still maintains that the higher numbers obtained by

Thomsen are due to heat carried over from the burner to the calorimeter (Abstr., 1886, 409), and suggests that the error in the case of benzene being 11,400 cal., the errors in the case of substances which have to be heated at 116° and higher must be still greater.

N. H. M.

Alcoholates of Sodium Glyceroxide. By De Forcrand (*Compt. rend.*, **104**, 291—294).—If a concentrated solution of sodium methoxide in absolute methyl alcohol is mixed with an equivalent quantity of glycerol, the mixture deposits an alcoholate of sodium glyceroxide, $C_3H_5(OH)_2{\cdot}ONa + MeOH$, in very deliquescent, white needles, which lose the whole of their methyl alcohol when heated at 120° in a current of dry hydrogen. It dissolves in methyl alcohol to the extent of 120 grams per litre at 15°. Heat of dissolution in water at 16° = −2·00 cal.

$C_3H_5(OH)_3$ liq. + NaHO solid + MeOH liq. = H_2O solid + $C_3H_5(OH)_2{\cdot}ONa$,MeOH solid	develops +17·06 cal.
$C_3H_5(OH)_2{\cdot}ONa$ solid + MeOH liq. = $C_3H_5(OH)_2{\cdot}ONa$,MeOH solid	„ + 5·04 „
$C_3H_5(OH)_3$ + MeONa diss. in *n*MeOH liq. = $C_3H_5(OH)_2{\cdot}ONa$,MeOH solid pptd. in *n*MeOH liq.	„ + 0·73 „
$C_3H_5(OH)_3$ + MeONa diss. in *n*MeOH liq. = $C_3H_5(OH)_2{\cdot}ONa$ solid + $(n+1)$MeOH liq.	absorbs − 4·42 „

It is evident that as in the case of the ethyl alcoholate the formation of the alcoholate is exothermic whilst that of the glyceroxide alone would be endothermic. The thermal disturbances which accompany the four corresponding reactions in the case of the ethyl alcoholate are respectively,

+16·60 +4·58 +3·92 −0·63.

The ethyl alcoholate of sodium glyceroxide dissolves in ethyl alcohol to the extent of 13 grams per litre at 15°.

The propyl alcoholate, $C_3H_5(OH)_2{\cdot}ONa$,PrOH, is obtained in a similar manner; one litre of propyl alcohol dissolves 7 grams at 15°. Heat of dissolution in water = −0·57 cal. The thermal disturbances corresponding with the four reactions already given are respectively,

+16·69 +4·67 +6·10 1·65 cal.

The isobutyl alcoholate is obtained in the same way; one litre of isobutyl alcohol dissolves 4·6 grams at 15°. Heat of dissolution in water = +1·23 cal. The thermal disturbances corresponding with the four reactions are respectively,

+14·73 +2·71 +14·89 − x +12·41 − x,

where x is the heat of dissolution of sodium isobutyl oxide in excess of isobutyl alcohol, which has not been determined, but is in all probability between +10 and +12 cal.

The amyl alcoholate dissolves in amyl alcohol to the extent of 28 grams per litre at 15°. Heat of dissolution in water +0·99 cal. The thermal disturbances corresponding with the four reactions are

$$+14{\cdot}82 \qquad +2{\cdot}80 \qquad +15{\cdot}02 - x \qquad +12{\cdot}41 - x,$$

where x has the same signification as in the case of the isobutyl compound. C. H. B.

Alcoholates of Potassium Glyceroxide. By De Forcrand (*Compt. rend.*, **104**, 361—364).—These alcoholates are compounds of potassium glyceroxide, $C_3H_7O_3K$, with one molecule of an alcohol of the paraffin series. They are obtained by adding one molecule of glycerol to a solution of one molecule of the potassium alkyl oxide in the corresponding alcohol. The following table gives the heats of dissolution of the alcoholates in water, the thermal disturbances corresponding respectively with the following reactions:—

(1.) $C_3H_8O_3$ liq. + HOK solid + ROH liq. = H_2O solid + $C_3H_7O_3K$,ROH solid.

(2.) $C_3H_7O_3K$ solid + ROH liq. = $C_3H_7O_3K$,ROH solid.

(3.) $C_3H_8O_3$ liq. + ROK diss. in nROH liq. = $C_3H_7O_3K$,ROH solid + nROH liq.

(4.) $C_3H_8O_3$ liq. + ROK diss. in nROH liq. = $C_3H_7O_3K$ solid + $(n+1)$ROH liq.

and the amount of the alcoholate dissolved by one litre of the corresponding alcohol.

	Heat of dissolution.	1.	2.	3.	4.	Solubility.
	cal.					grams.
Methyl alcoholate ..	−1·48	+19·49	+3·65	+2·54	−1·22	400
Ethyl „ ..	—	+18·53	+2·69	+3·17	+0·46	187
Propyl „ ..	−0·67	+19·60	+3·76	+5·79	+1·89	158
Amyl „ ..	+1·05	+17·62	+1·78	+6·28	+4·47	40

Isobutyl alcohol forms no alcoholate with potassium glyceroxide; with this exception, all the monhydric alcohols behave in the same way. The formation of the alcoholate is exothermic, but the quantity of heat developed, with the same metallic derivative, decreases as the molecular weight of the alcohol increases. For the same alcoholate, the heat developed diminishes as the atomic weight of the metal in the glyceroxide increases. The solubility of the alcoholates in the corresponding alcohol also diminishes as the molecular weight increases. C. H. B.

Heat Equivalents of the Homologues of Benzene. By F. Stohmann, P. Rodatz, and W. Herzberg (*J. pr. Chem.* [2], **35**, 40—42).—These investigations presented considerable difficulties

which made it desirable to check the results of observations, the difficulties being principally due to the impurity of the substances employed although subjected to repeated fractional distillation. Benzene constitutes an exception, as it may be purified by fractional solidification. The results of combustion of the successive homologues show such inconstancy of difference that it can only be accounted for by impurity of the hydrocarbon employed. The results are, however, capable of being checked by comparing them with those obtained by calculation from three distinct methods, namely:—(1) Starting from benzene and employing the formula $x = -H + CH_3 + 156000$ cal.; (2) from the mean values obtained for the liquid phenols from the formula $C_6H_6 = C_6H_5{\cdot}OH + 53600$ cal.; and (3) from the mean value of the phenol ethers according to the formula $C_6H_6 = C_6H_5{\cdot}O{\cdot}CH - 121700$ cal. The mean results obtained from these calculations agree within 0·6 per cent. with those obtained by experiment.

	Calculated.	Found.
Benzene	779·5 cal.	779·5 cal.
Toluene	935·6 „	933·8 „
Xylene	1091·4 „	1084·2 „
Cumenes	1247·7 „	1251·7 „
Cymenes	1404·8 „	1401·6 „

A. H. F.

Heat Equivalent of Ethers of the Phenol Series. By F. Stohmann, P. Rodatz, and W. Herzberg (*J. pr. Chem.* [2], **35**, 22—39).—1. Phenol Ethers.—*a. Anisoïl*, OPhMe. This was rectified by a distillation between 152° and 153°, the pressure being about 755 mm. Five determinations were made of the heat of combustion, giving mean values of 8345 cal. per gram, or 901282 cal. per molecular equivalent. *b. Phenetoïl*, OPhEt, rectified between 166·5° and 167·5°. A mean of nine determinations gave the heat of combustion as 8666 cal. per gram, or 1057225 per molecular equivalent. *c. Phenyl propyl ether*, OPhPrα. This was made by distilling together normal propyl bromide with alcoholic solution of potassium phenoxide, separating the product subsequently from water, washing with aqueous potash, drying, and redistilling. The boiling point was then constant at 185·2° under normal pressure, and the ether so obtained gave 8922 cal. per gram, or 1213426 per molecular equivalent. Experiments were made on higher members of the series, but not with sufficiently concordant results for figures to be given.

2. *Cresol Ethers.*—Two of these were examined, namely, meta-cresyl methyl ether, $C_7H_7{\cdot}OMe$, and paracresyl ethyl ether, $C_7H_7{\cdot}OEt$, and were found to have heat-equivalents almost identical with their isomerides of the previous group, namely, 8666 and 8920 cal. respectively.

3. *Xylenol Ethers.*—Two of these were examined, namely, xylyl methyl ether (1 : 3) and xylyl ethyl ether (1 : 4).

4. Two thymyl ethers were experimented on, and finally two ethers obtained by substitution of methyl for hydrogen in resorcinol and quinol.

Comparison of the results for this series of ethers shows that the

introduction of a methyl-group corresponds with an increase of 155900 cal., whether the methyl-group enters the phenyl- or the methyl-group. Also the heat of formation is found to rise uniformly by 7100 cal. for each successive homologue.

These results agree closely with those obtained from examination of allied groups, namely, the alcohols and the phenols; the former giving 156163 cal. the latter 156356 cal. as the equivalent of the methyl-group.

From these experiments, calculations were made on the heat value of the methoxyl-group in these ethers ($x = -H + OCH_3$); thus, for liquid benzene 779530 cal., for phenyl methyl ether 901282, and for dimethylresorcinol 1022966 cal., these corresponding with successive additions of $CH_2{\cdot}O$, of which the equivalent is 121718 cal.

The latter part of the paper is concerned with deductions from the foregoing experimental results. First it is observed that similarly constituted isomeric substances have practically the same heat-equivalent, for instance, resorcinol, catechol, and quinol; or the ortho-, meta-, and para-cresols. Secondly, it is seen that isomerides if belonging to different chemical groups have markedly different heat-equivalents; thus the heat-equivalent of phenyl methyl ether is 901282 cal., whilst that of any one of the metameric cresols is 882288 cal. Similar results were obtained for other metameric bodies.

Finally the heat of formation of the phenyl ethers was calculated by subtracting the sum of the heat-equivalent of one molecule of phenol and of alkyl alcohol from that of the ether. Calculated in this way, the values for the different homologous and isomeric ethers were found to be practically constant, and equal to −6720 cal. Slight differences for two of these ethers are accounted for by the difference falling well within the limits of experimental error, considering the nature of the calorimetric method employed.

The ethers of dihydroxybenzenes give similar results, the calculation, however, being somewhat complicated by the difference of physical condition of the reacting substancee and the product. Dimethylresorcinol gives −6824, and dimethylquinol −3412 cal. for their heat of formation. A. H. F.

Relation between the Critical Temperatures of Substances and their Thermal Expansions as Liquids. By T. E. Thorpe and A. W. Rücker (*Phil. Mag.* [5], **21**, 431—434), and by A. Bartoli and E. Stracciati (*ibid.*, 533—534).—Controversial papers in relation to Mendéleff's formula (compare Thorpe and Rücker, Trans., 1884, 135).

Specific Heats of the Vapours of Acetic Acid and Nitrogen Tetroxide. By R. Threlfall (*Phil. Mag.* [5], **23**, 223—224).—The author contends that the values obtained by Berthelot and Ogier for the specific heats of vapours of acetic acid and nitrogen tetroxide (Abstr., 1883, 6) support the theory of the dissociation of these gases. He further compares the specific heats of these vapours where the temperature coefficient is large with those of nitrous oxide and carbonic anhydride where the temperature coefficient is small, and argues that the usual formulæ for these gases only expresses the con-

stitution of the large majority of the molecules, whilst others of greater and less complexity also exist. With rise of temperature, dissociation proceeds, and an increased absorption of heat takes place.

H. K. T.

Influence of Change of Condition from the Liquid to the Solid State on Vapour-pressure. By W. Ramsay and S. Young (*Phil. Mag.*, **23**, 61—68).—Fischer (*Ann. Chim. Phys.* [2], **28**, 400) has stated that although he found the pressure of vapour in presence of water and in presence of ice identical at the melting-point of the latter, yet this was not the case with benzene. The authors have found that Fischer's statement, which is opposed to the second law of thermodynamics, is based on a wrong interpretation of his own results; for Fischer applied a formula of the form $p = a + bt + ct^2$, which is not adapted to express the relations of the temperatures and pressures of saturated vapours, instead of the formula devised by Biot and employed by Regnault, $p = a + b\alpha^t + c\beta^t$, and, moreover, did not make use of his own results at low temperatures. On recalculating from Fischer's results by means of the latter formula the vapour-pressure of liquid and solid benzene at the melting point of the latter, it is evident that the values are identical. The authors have also redetermined these constants for benzene, and confirm Fischer's results as regards the liquid; but their results do not quite agree with Fischer's as regards the solid. By making use of Regnault and Schiff's determinations of the heat of volatilisation of benzene, Petersen and Widmann's and Fischer's number for the heat of fusion of solid benzene, Schiff's formula to express the specific heat of liquid benzene, and Fischer's determination of the specific heat of solid benzene, it is possible to bring a check to bear on the value of Fischer's and the authors' experiments. The result proves that the balance of evidence is in favour of the authors' determinations of the pressures of benzene vapour in contact with the solid.

W. R.

Nature of Liquids, as shown by a Study of the Thermal Properties of Stable and Dissociable Substances. By W. Ramsay and S. Young (*Phil. Mag.*, **23**, 129—138).—The authors refer to previous memoirs (*Phil. Trans.*, i, 1884 and 1886, and *Chem. Soc. Trans.*, 1886, 790), in which they have shown that whilst the density of the saturated vapours of stable substances, such as ethyl alcohol and ethyl ether, becomes normal at low temperatures and correspondingly low pressures, those of acetic acid, and, as is shown by results lately published by the Messrs. Natanson, also those of nitric peroxide, increase with fall of temperature. It is held by many chemists that gaseous molecules, in changing to liquid, form molecular groups of definite complexity, exercising cohesive attraction on each other; on the other hand, it is conceivable that the liquid condition is a purely physical one, and that a liquid consists of molecules similar in every respect to those of a gas, but, owing to their closer proximity, exhibiting only that form of attraction known as cohesion. The arguments which have led the authors to adopt the latter view as correct are, that it is difficult to conceive that the rise of density of the saturated vapour of acetic acid, both at high and at low temperatures, can be

due to the same cause, for at high temperatures the conditions are unfavourable to chemical combination, but owing to the necessarily high pressure, the molecules are in close proximity, and the substance exhibits a high vapour-density; whereas at low temperatures the conditions are favourable to chemical combination, whilst the molecules, owing to the corresponding low pressures, are very far apart; so that cohesive attraction is out of the question. With alcohol and ether, a rise of density does not accompany fall of temperature; but at high temperatures they exhibit that rise of density common to all substances, stable or dissociable. Hence it is argued that there is no combination of the nature termed "chemical," that is elective, in the case of stable liquids; each molecule exerts cohesive attraction on all within its influence, but does not single out any small number of other molecules with which to combine. The authors also call attention to the fact observed by them that while the vapour and liquid of a stable substance exist in a closed space in presence of each other, pressure remains absolutely constant through the widest possible changes of volume; but with dissociable substances the pressure rises somewhat as volume is decreased, thereby revealing the partial formation of more complex molecules during the act of condensation. It is shown that the thermodynamical formula suggested by Willard Gibbs to represent the dependence of dissociation on pressure and temperature, does not represent facts at high temperatures in the case of acetic acid. The conclusion at which the authors arrive is that the difference between liquids and gases is one of degree, not of kind; is quantitative, and not qualitative. W. R.

Apparatus for Determining Vapour-densities. By G. Dyson (*Chem. News*, **55**, 88).—The apparatus described is a modification of Victor Meyer's apparatus, and is arranged, by means of a manometer attached to it, to read the pressure produced by the volatilisation of a known weight of substance in a space of known capacity.

D. A. L.

Thermodynamics and Chemistry. By H. Le Chatelier (*Bull. Soc. Chim.*, **46**, 737—746).—The writer considers the conditions of equilibrium of a gaseous mixture, such as a mixture of hydrogen, oxygen, and water at temperatures and pressures such that the water is partially dissociated. If we denote by N the number of molecular weights of the various substances existing in the mixture, this number will be a measure of the degree of dissociation, and will depend on two other quantities only, namely, the pressure P and the temperature T. Between these three quantities, there must exist a relation of the form $F(N,P,T) = 0$, which is the law of equilibrium of the system under consideration. The form of this function cannot be directly determined, but if we suppose a surface to be described representing the nature of the function for any particular system, then the sections of this surface made by three planes perpendicular to each of the coordinate axes respectively, will give us three distinct curves. The one in which the temperature remains constant is an *isothermal*, that in which the pressure is constant is an *isobar*, and the third is a *curve of equal dissociation*. By applying the second law of thermodynamics

and assuming the correctness of Boyle's and Gay-Lussac's laws, the author obtains the differential equation to the curves of equal dissociation, and points out that the equation contains no coefficient depending on the proportions of the substances initially present in the mixture.

It also appears that the sign of the change of pressure consequent on elevation of temperature depends on the sign of the latent heat of reaction of the system.

In general, it is easy to calculate or study experimentally the equations to the isothermals and isobars; and when these are known, the form of the function can be determined. The author applies this method to several cases, including saturated vapours, liquids in presence of soluble gases, and the dissociation of gaseous mixtures. In many cases (for instance, the vapour-tension of mixed liquids), the forms of the isothermals are not known with sufficient accuracy to admit of calculation. The author criticises severely the manner in which the principles of thermodynamics have been applied by some writers to the study of chemical phenomena, and points out the uncertainty of the assumption made in W. Gibbs's mathematical theory, namely, that the entropy of a mixture of gases is equal to the sum of the entropies of its constituents. L. T. T.

Representation of the Connection between the Gaseous and Liquid States of Matter by Isopyknics. By S. v. Wroblewski (*Ann. Phys. Chem.* [2], **29**, 428—451).—All former researches on this subject were based on investigations of the isothermal, a curve which gives the relation between pressure and volume at different temperatures. Jamin (Abstr., 1884, 5) has recently substituted for volume its reciprocal density. The author proposes the following:—Suppose a mass of gas or liquid of any definite density; when the temperature is changed, the pressure must also be changed in order to keep the density constant. The curves which represent the relation between pressure and temperature for different densities are named *isopyknics* (from *ἴσος πυκνός*). If a system, of such curves be drawn for any homogeneous isotropic substance, these curves can nowhere intersect each other.

Such a system has been constructed by the author for carbonic acid by means of Sarrau's formula (Abstr., 1886, 203), which is taken as most nearly representing the experimental results. The curve corresponding to density d, of which the values of T (absolute temperature) are abscissæ, and of p (pressure in atmospheres) ordinates, is called for brevity the isopyknic d. A diagram is given showing the course of the isopyknics from $d = 0{\cdot}025$ to $d = 1{\cdot}2$ for temperatures up to $T = 370°$ and $p = 400$ atmospheres; and on the same diagram is drawn the curve of minimum values of pv. For temperatures below 30°, this is of course identical with the curve of liquefaction. This portion has been calculated from the data of Regnault and of Pictet (*Ann. Chim. Phys.* [5], **13**, 213); it is slightly *convex* towards the axis of temperature. The upper part of the curve, which is slightly *concave* towards the axis of T, has been calculated from the experiments of Amagat (*ibid.* [5], **22**, 374) from 35° to 100°.

There is thus a gap in the middle of this curve (named by the author "principal curve") for which observations are either wanting or untrustworthy; and here the point of inflection would evidently occur. The general aspect of this curve is that of a slightly wavy line, from various points along which the isopyknics radiate; those proceeding from the lowest points being nearly parallel to the axes, and those from the critical point onwards being nearly parallel to the principal curve. Inspection of the diagram leads to some new conclusions.

Sarrau's equation gives good results for the higher pressures, but is unusable in the neighbourhood of the curve of liquefaction, since here it allows the isopyknics to pass through and intersect each other. The true course of an isopyknic would probably be that it would bend slightly on approaching the curve of liquefaction and thenceforward run downwards close beside it. Thus all isopyknics should collect into a bundle in this region. Such a course, however, is not indicated by Sarrau's equation. In the neighbourhood of the critical point, the densities of liquid carbonic acid measured by Andreew (*Annalen*, **110**, 1) are much higher than those calculated by Sarrau. Although Andreew's observations are untrustworthy, it is probable that here Sarrau's values are too low. In other cases, too, Sarrau's equation leads to impossible results.

By moving along an ordinate in the diagram, we change from one isopyknic to another by simple change of pressure; but by moving along an abscissa the same thing is effected by change of temperature. Thus the passage from one isopyknic to another in a vertical or a horizontal direction gives a conception of the compressibility of the substance, or of its expansion by heat.

Now, according to Andrews' conception, everything on the diagram above the curve of liquefaction, and within the ordinate of so-called "critical temperature," indicates *liquid;* everything outside these limits, *gas.* The author believes, however, that the two states are separated, not by the ordinate in question, but by the principal curve, or the curve pv = minimum. Everything below this indicates *gas;* everything above it, *liquid.* His reasons are as follows.

In the first place, the rate of change of density with pressure $(d_1 - d)/(p_1 - p)$ when dp and $d_1 p_1$ refer to neighbouring isopyknics, changes uniformly from below upwards, whether to right or left of the ordinate of critical temperature. The values of this quotient for different absolute temperatures are given in a table, and in each case they first increase, then reach a maximum, and then begin to decrease. If the curves of equal values of $(d_1 - d)/(p_1 - p)$ are drawn, they are, like the principal curve, convex below and concave above, towards the axis of temperature. So also over the whole diagram this quotient slowly diminishes with increase of temperature.

Again, the coefficient of compressibility, $K = \frac{1}{v} \cdot \frac{v_1 - v_2}{p_2 - p_1}$, has constantly diminishing values for increase of temperature, when always calculated between neighbouring isopyknics; but constantly increasing values for increasing temperature when the pressure is kept constant. Carbonic anhydride is thus more compressible at high than at low temperatures. And, finally, the coefficient of expansion

by heat $(d - d_1)/d_1(t_1 - t)$ under different pressures points to no specific difference between the regions on each side of the critical ordinate. In no case, therefore, is any *discontinuity* observed at this ordinate. It has then no special significance, and the conception of critical temperature as that above which liquefaction of a gas is impossible is erroneous and only an obstacle to progress. The same is true of Mendeléeff's conception (O. E. Meyer, *Kinetische Theorie der Gase*, p. 64).

Andrews' conception was based on the absence of a meniscus at any temperature above 30·92° and the forms of the isothermals. But, as Jamin has pointed out, the absence of the meniscus is simply due to the approximately equal densities of the gas and liquid at the critical point; hence the formation of liquid cannot be *seen*.* These conditions are well seen in the diagram. At the critical point, the isopyknics 0·4 and 0·5 approach opposite sides of the curve of liquefaction. At higher points, the densities on opposite sides of the principal curve differ still less.

The forms of the isothermals also prove nothing. For since the difference between the densities of the liquid and of the saturated vapour above it is exceedingly small above the critical temperature, there is here no cause for the *bending* which in the lower isothermals denotes liquefaction. This bending is, in fact, due to difference of density.

It is commonly asserted that from the critical point upwards there is no latent heat; and it might be objected to the author's view, that if there is no difference of density no heat can be necessary to produce a change of state; there can then be no liquid state above the critical temperature. The author meets this objection by quoting some of his own experiments on the liquefaction of nitrogen (*Ann. Phys. Chem.* [2], **25**, 398), in which the passage of the liquid to the state of gas at the critical point was certainly attended by absorption of heat. Such a change could not be brought about without either absorption of heat or diminution of pressure.

It is to be noted that the isopyknic 0·05, which corresponds nearly with the density of liquid carbonic anhydride at the critical point, comes very close to the upper branch of the principal curve; and when our knowledge of carbonic anhydride is more accurate, it may be found to coincide with it. Every point on this isopyknic from 30·92° upwards, might be regarded as "the critical point." For Andrews' conception, "critical temperature," it would be better to substitute the conception "critical density," or the least density which the substance can have as a liquid. The corresponding isopyknic would then be named "critical isopyknic."

The author dwells on the great difficulty in determining the precise conditions under which the meniscus really disappears. Disregard of this has led Cailletet (Abstr., 1880, 604) and Van der Waals to assert that by increased pressure the liquid could be made to dissolve in the gas above it.

* This view was first advanced by Ramsay, *Proc. Roy. Soc.*, **30**, 323.—Ch. B.

Stefan has lately shown that when a liquid exists under the pressure of its saturated vapour, and whilst a meniscus is distinctly visible, there must nevertheless be a gradual transition between the gas and the liquid at the boundary. The diagram represents this perfectly. For although the gas and liquid are both under the same pressure, and the points on the diagram corresponding with the two states are immeasurably close together, these points are still on opposite sides of the principal curve, and between them all the isopyknics for intermediate densities must pass down. A particle of liquid, then, to reach the other side of the curve must pass through all these intermediate states. A meniscus is, however, visible because the transition layer is exceedingly thin. CH. B.

Specific Gravities of Mixtures of Ethylic Alcohol and Carbonic Anhydride. By A. BLÜMCKE (*Ann. Phys. Chem.* [2], **30**, 243—250).—The author has determined the specific gravities of mixtures of alcohol and carbonic anhydride at different temperatures and pressures, by a slightly modified form of the method already described (Abstr., 1885, 215). The following are the results, the figures in column *p* denoting the percentages of carbonic anhydride in the mixtures:—

	0·4°. P = 35 atmos.	17°. P = 55 atmos.	25°. P = 66 atmos.
p.	Specific gravities.		
0	0·810	0·795	0·790
10	0·826	0·808	0·799
20	0·841	0·822	0·808
30	0·858	0·835	0·818
40	0·874	0·848	0·827
50	0·890	0·859	0·836
60	0·899	0·870	0·845
70	0·916	0·876	0·852
80	0·925	0·877	0·844
90	0·931	0·871	0·830
100	0·934	0·841	0·728

The specific gravity thus reaches a maximum for 80 per cent. of carbonic anhydride under 55 atmospheres pressure, and for 70 per cent. under 66 atmospheres. No relation between the specific gravities of the constituents and that of the mixture has been discovered.

A table is also given showing the increase of volume produced in alcohol by addition of carbonic anhydride. If the new volume of 1 c.c. of alcohol, $V = 1 + na$, where n equals the number of c.c. of gaseous carbonic anhydride at 0° and 760 mm., the value of a is approximately constant for mixtures containing less than 50 per cent. of carbonic anhydride; and for a mixture of this strength = 0·00199 at 0·4°,

0·00210 at 11°, and 0·00221 at 25°. For greater proportions of carbonic anhydride, a increases, especially at the higher temperatures.

The author's values for the specific gravity of liquid carbonic anhydride ($p = 100$ in the table) at the liquefying pressure are different from those observed by Andreew (*Annalen*, **110**, 1) and those calculated by Clausius' and Sarrau's equations. Andreew found 0·947 at 0°, 0·849 at 17°, 0·783 at 25°.

These measurements were however made by compressing carbonic anhydride in glass tubes and calculating the uncondensed gas on the basis of Boyle and Marriott's law, which does not hold near the critical temperature. The author's results are also different from those recently obtained by Cailletet and Matthias (Abstr., 1886, 758), namely, 0·908 at 0°, 0·842 at 10°, 0·748 at 20°.

The carbonic anhydride used by the author may have been slightly impure. CH. B.

Dissociation of Sodium Phosphate and the Measure derived from the Vapour-tension of the Chemical Attraction of the Water of Crystallisation. By W. MÜLLER-ERZBACH (*Ber.*, **20**, 137—141).—The results of two series of experiments made with disodium hydrogen phosphate show that within the limits of temperature of 13° and 62° the chemical attraction between sodium phosphate and its water of crystallisation has a constant or nearly constant value. With a considerable rise of temperature, the attraction must become slighter, owing to the increased distance of the components, so that the greater dissociability of strongly heated salts is readily explained. The behaviour of water absorbed by alumina (*Ann. Chim. Phys.* [2], **28**, 695) makes it probable that greatly diminished chemical affinity will be found only at a temperature considerably above 62°. N. H. M.

Solubility of Solid Substances, and the Changes in Volume and Energy accompanying Solution. By F. BRAUN (*Ann. Phys. Chem.* [2], **30**, 250—274).—Let p be the pressure, t temperature, V volume, and E total internal energy, all in absolute units, of the mixture of a solid salt with its saturated solution; and let dQ be the quantity of heat added for an infinitesimal change of p and t; then

$$JdQ = pdV + dE = \left(p\frac{V}{\delta p} + \frac{\delta E}{\delta p}\right)dp + \left(p\frac{\delta V}{\delta t} + \frac{\delta E}{\delta t}\right)dt,$$

where J = mechanical equivalent of heat. Let r be the mass, v specific volume, m coefficient of compression, a coefficient of expansion by heat, and u internal energy per unit mass, of the solution; and let ρ, ϕ, μ, α, and ω be the similar magnitudes for the solid salt. Then v is directly changed by the pressure, and indirectly by the further solution (or deposition) of salt. Hence $dv/dp = \delta v/\delta p + \delta v/\delta\gamma \,.\, \delta\gamma/\delta p$, when γ is a magnitude depending on the amount of salt initially in solution, and the partial differential coefficients refer only to the first part of the change; so also for $\delta v/\delta t$, $\delta u/\delta p$, and $\delta u/\delta t$. The total change of V due to pressure alone will then be

$$\frac{\delta V}{\delta p} = r\frac{\delta v}{\delta p} + \rho\frac{\delta \phi}{\delta p} + \nu \,.\, \epsilon\phi r,$$

where ϵ = the mass of salt which dissolves in 1 gram of solution when the pressure is increased by unity, and ν = coefficient of contraction of this salt in dissolving. In a similar way,

$$\frac{\delta V}{\delta t} = r\frac{\delta u}{\delta t} + \rho\frac{\delta \phi}{\delta t} + \nu \,.\, \eta\phi r,$$

where η = mass of salt which dissolves in 1 gram of solution saturated at $t°$, when the temperature is raised 1°.

Again since at pressure p, $E = ur + w\rho$, at $p + dp$, the total internal energy $= E + \delta E/\delta p \,.\, dp$, by partial differentiation with respect to p and to t, and putting $\delta\gamma/\delta p = x\epsilon$ and $\delta\gamma/\delta t = x\eta$, we find,

$$\frac{\delta E}{\delta p} = r\frac{\delta u}{\delta p} + \rho\frac{\delta w}{\delta p} + \left(u - w + x\frac{\delta u}{\delta \gamma}\right)\frac{\delta r}{\delta p}.$$

$$\frac{\delta E}{\delta t} = r\frac{\delta u}{\delta t} + \rho\frac{\delta w}{\delta t} + \left(u - w + x\frac{\delta u}{\delta \gamma}\right)\frac{\delta r}{\delta t}.$$

Here we may write $u - w + x\delta u/\delta\gamma = -J\lambda$, where λ = the heat absorbed when 1 gram of salt dissolves in its nearly saturated solution, neglecting external work. Then by substitution in the first equation, and putting $p\delta v/\delta p + \delta u/\delta p + T\,\delta v/\delta t = 0$, and $p\delta\phi/\delta p + \delta w/\delta p + T\,\delta\phi/\delta t = 0$, since dQ/T must be an exact differential, we get finally

$$\epsilon(J\lambda - p\nu\phi) = T\nu\eta\phi.$$

In this expression $\lambda - p\nu\phi/J = L$, the latent heat of solution at pressure p, including external work.

This equation shows that—first, substances which dissolve in their nearly saturated solutions with development of heat and diminished volume, must have their solubility increased by pressure; second, substances which dissolve either with absorption of heat or with increased volume, must be partly precipitated by pressure. Other interesting relations follow from it.

Sorby (*Proc. Roy. Soc.*, **12**, 538), reasoning from the change of melting point by pressure, has already been led to experiment in this direction, and found for sal ammoniac, which dissolves with increased volume, diminished solubility at high pressures; but for sodium chloride, copper sulphate, potassium sulphate, and potassium ferro- and ferri-cyanide, which dissolves with contraction, increased solubility at high pressures. Möller also (*Ann. Phys. Chem.* [1], **117**, 386), has made similar experiments; his results partly contradict those of Sorby.

In the experimental part of his work, the author has used a cast-iron block pierced lengthwise by two narrow communicating channels, which could be closed by steel screws with copper washers. In one of these pressure was produced by a copper plunger, forced in by a screw and lever; the other contained the solution or mixture experimented on. The pressure applied, about 900 atmospheres, was

estimated in a preliminary experiment from the amount of mercury forced into a capillary tube containing water, and opening into mercury. The iron block was placed in a bucket of ice, or of water surrounded by ice. All experiments were made with solutions carefully saturated at 0°. Pressure was applied in each case for varying times, and the gain or loss of salt estimated from the specific gravity of the solution.

Full authorities are given for the constants used in the calculations. The more important are as follows: Sal ammoniac. $L = -34{\cdot}4$, $\nu_0 = 0{\cdot}356$; and if $\bar{\epsilon}$ = quantity of salt which goes into the saturated solution when the pressure is raised 1 atmosphere, $\bar{\epsilon} = -0{\cdot}000125$. The saturated solution must therefore be partly precipitated by pressure.

Sodium chloride. λ (determined by the author) $= -2$, and $\nu = -0{\cdot}177$. Here $\nu = -0{\cdot}177$ varies with the pressure, at 1530 atmospheres becoming $= 0$ (see later). For 100 atmospheres $\bar{\epsilon} = 0{\cdot}000062$.

Alum. $\lambda = -12$, and $\nu = -0{\cdot}1033$. $\bar{\epsilon} = 0{\cdot}0001648$.

Sodium sulphate ($Na_2SO_4 + 10Aq$). $\lambda = -187$, $\nu = -0{\cdot}1496$ and $\bar{\epsilon} = 0{\cdot}0000351$.

The three last, therefore, must show increased solubility at high pressures.

The experimental results were as follows: Saturated alum solution dissolved, after 23 hours, 1·1; after 20 hours, 1·8; after 18 hours, 1·3; after 18 hours, 2·9; after 3 hours, 3·27 grams per 100 grams of solution. The greatest change thus corresponded with a pressure of 200 atmospheres, the pressure having evidently fallen off as a result of contraction. Sodium sulphate solution dissolved, after 20 hours, 1·57, and, after 19 hours, 0·92 gram per 100 of solution. The greatest change here corresponded with 500 atmospheres. Sodium chloride solution dissolved, after 36 hours, 0·32, after 28 hours, 0·32 gram per 100 of solution. On the other hand, sal ammoniac solution *deposited* 2·18 grams per 100 of solution after 38 hours. A fall of 10° in temperature would be required to produce the same change.

The author has also measured the compressibilities of the salts given below, and of the saturated solutions, by means of Oersted's piezometer. The coefficients were first measured for the solutions,

Coefficients of Compressibility.

	Volume.		Specific gravity.		Coefficient of comp.	
	Salt.	Solution.	Salt.	Solution.	Salt.	Solution.
NH_4Cl.....	7·69 C.³	22·99 C.³	1·533	1·073	$4{\cdot}9\times10^{-6}$	$38{\cdot}0\times10^{-6}$
Alum (cryst.)..	17·65	13·76	1·724	1·03	$1{\cdot}9\times10^{-6}$	$46{\cdot}0\times10^{-6}$
NaCl.....	12·25	19·23	2·15	1·212	$1{\cdot}4\times10^{-6}$	$27{\cdot}0\times10^{-6}$
$Na_2SO_4,10H_2O$	19·1	11·54	1·465	1·045	$7{\cdot}1\times10^{-6}$	$42{\cdot}5\times10^{-6}$

and subsequently from the compressibilities of mixtures of salt and solution; the constants were calculated for the solids. The unit of pressure is one atmosphere, temperature 1°.

As a rule, solution is attended by contraction; ammonium chloride, bromide, and iodide, magnesium chloride and tartaric acid, furnish the few known exceptions at ordinary temperatures and pressures. Under other conditions, the final volume of a solution may be assumed to be the same whether the water and salt are separately compressed before mixture, or compressed after mixture; and it may be shown that the rate at which the coefficient of contraction changes with pressure, or $\delta\nu/\delta p$, will be negative, nothing, or positive, accordingly as the change of volume of a solution by pressure is $> = <$ the change of volume of the components. Now for the four solutions investigated, the sum of the compressibilities of the components is always considerably greater than that of the mixture. Three cases are then possible:—1st. The water in the solutions may regain its compressibility in the free state. Evidently then the dissolved salts must expand on compression, which is hardly probable. 2nd. The salts in solution may retain the above determined compressibilities. 3rd. The salts may behave as though incompressible. In either of the latter cases, it can be seen from the table that the compressibility of the water in the solution must be much less than that of pure water ($= 51 \times 10^{-6}$). In all cases, the effect of solution has therefore been to make the water more *rigid;* and since $\delta\nu/\delta p$ is always positive, the attraction attending solution must diminish, and the dilatation increase, with increased pressure. Again, since for all easily soluble salts, at least up to 50°, the coefficient of expansion by heat of a saturated solution is greater than that of a less saturated solution, or of the solid salt; it can easily be shown that $\delta\nu/\delta t$ is likewise positive. Thus the changes of volume accompanying solution, whether produced by rise of temperature or by increased pressure, always tend toward expansion.

The author shows also that λ must always change in the same sense both with increasing pressure and increasing temperature. The experiments of Winkelmann prove that λ diminishes at high temperatures. With increasing temperature and pressure, it must, therefore, diminish rapidly; and the author suggests that the solution of a solid might mix with the solvent heated above its critical temperature, as soon as λ becomes $= 0$.

Is the variation of solubility with temperature due to a change of molecular forces, or to a specific influence of heat? It is conceivable that thermal expansion may alter the molecular forces by changing the distance between the molecules. But in this case all substances which go into solution with diminished volume should be partly precipitated by warming their saturated solutions, which is contrary to experience. The influence of heat on solubility is therefore *specific*, although its exact nature is as yet undecided. Regarding the volume changes due to pressure and to temperature as having equal effect on solubility, the author calculates that the increase due to a specific heat influence alone is equal to the actual increase multiplied by 1·107 for alum; by 1·016 for sodium sulphate; by 4·8 for sodium

chloride; and by 0·596 for sal ammoniac. For sodium chloride, the diminution of solubility due to molecular forces is insignificant when compared with the increase directly due to heat. For ammonium chloride both influences work in the same direction. Ch. B.

Liquid Diffusion. By J. J. Coleman (*Phil. Mag.* [5], **23**, 1—10). Determinations of velocity of diffusion were made by Graham's jar method, and by a burette method in which the solutions were introduced, and the different strata drawn off through the tap at the bottom. The rates of diffusion of mercurous nitrate, mercuric chloride, lithium sulphate, cadmium sulphate, silver sulphate, manganese sulphate, nickel sulphate, and lead nitrate were determined.

The author finds that the velocities of liquid diffusion of the elements vary in a manner similar to that of their atomic volumes, being less for elements at the centre than for those at the ends of the horizontal series in the periodic arrangement. Thus calcium chloride is less diffusible than potassium chloride, and strontium chloride less diffusible than potassium and rubidium chlorides, which have the same diffusive velocity. In this last case, the author supposes that the effect of the large molecular volume of the rubidium chloride is neutralised by the greater molecular weight. In order to examine this point, the author diffused solutions of magnesium and zinc sulphates, which have equal molecular volumes, for 50 days. The magnesium sulphate proved the most diffusive. In the same way, chromic acid was found to be more diffusive than tungstic acid.

The author further considers the equal diffusibility of the chlorides, bromides, and iodides of potassium and sodium, to be due to the neutralisation of the effect of increase of molecular volume by that of increase in molecular weight. The diffusion rate of the sulphates of the 8th periodic group were the same as that of the 2nd or dyads, whilst the monads contrast strikingly with the latter. H. K. T.

Catalytic Actions. By O. Loew (*Ber.*, **20**, 144—145).—When a 15 per cent. solution of formaldehyde is mixed with an equal volume of concentrated aqueous soda, a slight evolution of gas takes place only on warming. The addition of cuprous oxide to the mixture causes an extremely violent evolution of hydrogen, accompanied by a moderate rise of temperature; sodium formate is produced. This evolution of gas could be produced by no other metallic oxide.

Hydroxylamine is very rapidly decomposed by caustic soda in presence of platinum-black. N. H. M.

Conditions of Equilibrium in Aqueous Solutions: Action of Aqueous Soda on some Normal Sodium Salts. By T. Thomsen (*J. pr. Chem.* [2], **35**, 145—161).—When sodium hydroxide is added to a solution of sodium hydrogen tartarate, the molecular rotary power at first increases, and reaches a maximum when the acid is completely converted into neutral salt (*J. pr. Chem.* [2], **34**, 81). Further addition of soda causes a diminution in the rotation, which varies both with the concentration of the solution and with the excess of alkali. Thus, if p = percentage of acid, and n = total number of

molecules of NaOH present in the solution, the initial molecular rotation, $(m)_D = 60{\cdot}6°$, of a weak solution of neutral salt ($p = 2$, $n = 2$) becomes 59·7° for $n = 5$. On the other hand, when $p = 18$, $n = 2$, the initial rotation, $(m)_D = 57{\cdot}58°$, becomes 18·57° when n is increased to 5. For solutions of intermediate strength, or for intermediate amounts of alkali, the loss of rotatory power lies between the above limits. Other alkalis (KOH, NH_3) produce a slight *increase* of rotation with increased concentration. The effects of the several alkalis are graphically represented by means of curves for the different values of n, of which the values of p are abscissæ, those of $(m)_D$ ordinates. These curves appear to converge to about the same point for low values of p.

The author explains these results by assuming that in weak solutions soda, even in excess, simply neutralises tartaric acid, but that when the concentration is great a new lævorotatory compound is formed, probably by displacement of the hydroxylic hydrogen of the acid. And, in fact, by very largely increasing the excess of alkali, the rotation is rendered left-handed. Thus, for a 6 per cent. solution of tartaric acid, to which 39 mol. NaOH had been added, $(m)_D = -38°$.

Very similar results are obtained with malic and quinic acids. The author has redetermined the molecular rotation of sodium malate. This salt crystallises with extreme difficulty from its syrupy solution, unless brought into contact with previously formed crystals, when it slowly separates as a tough mass of the formula $Na_2C_4H_4O_5 + 4H_2O$. The table refers to the anhydrous sodium salt.

P.	*d*.	$(m)_D$.	P.	*d*.	$(m)_D$.
59·2	1·4825	+6·79°	33·9	1·2525	− 5·8°
57·43	1·4615	+5·96	29·93	1·2200	− 7·56
53·31	1·4270	+4·22	25·85	1·1880	− 9·19
47·75	1·3725	+1·21	20·00	1·1425	−11·04
42·9	1·3320	−1·38	15·00	1·1040	−12·36
36·69	1·2750	−4·52	—	—	—

These values differ somewhat, especially for strong solutions, from those found by Schneider (Abstr., 1881, 892). The rotation is thus different in weak and in strong solutions. Excess of soda invariably causes the solution to become more dextrorotatory. For example, excess of 1 mol. NaOH added to a solution containing 14·48 per cent. of malic acid as neutral sodium salt, reduces the molecular rotation from −11·24° to −7·21°; while excess of 3 mol. of alkali changes the rotation of a 20·5 per cent. solution from −861° to +19·12°. In this case also, the concentrated alkali probably acts on the hydroxyl-group.

Results of the same kind were obtained with quinic acid, which is monobasic but contains four hydroxyl-groups. On the other hand, the right-handed rotation of camphoric acid, which contains no hydroxyl-groups, was not sensibly affected by excess of soda.

The rotation of strong solutions of tartrates varies considerably

with the nature of the base. But by investigating the effect of dilution in each case, it is possible to calculate the molecular rotation for an infinitely dilute solution. Applying this method to the neutral potassium, sodium, and ammonium tartrates, the author shows that the limiting values thus obtained are approximately the same in the three cases, although the molecular rotations for strong solutions are very different. Similar limiting and nearly constant values may be calculated from Schneider's observations on the alkaline malates, and Landolt's on the alkaline quinates.

The author has already shown (Abstr., 1881, 147 and 257) that the molecular rotations of the carbohydrates in aqueous solution tend towards simple multiples of a constant as the dilution is increased; and the same holds for alcoholic solutions of the cinchona alkaloïds. In all cases which have been carefully examined, heat acts in the same sense as dilution, and doubtless the action in both cases is of a chemical nature; a conclusion strengthened by the fact that when the rotation of a tartrate is changed from right to left by heat, the transition is perfectly regular (Abstr., 1881, 911).

The polarimetric method can probably be applied to determine the distribution of a base between several acids in solution. Ch. B.

Lecture Experiments. By A. Valentini (*Gazzetta*, **16**, 399—401).—In this paper forms of apparatus are described, to show the synthesis of ammonia by the passage of nitrogen and hydrogen over a platinum spiral rendered incandescent by an electric current, and for attaining continuously a flame of nitric oxide and carbon bisulphide.

V. H. V.

Inorganic Chemistry.

Method for Obtaining Chlorine from Chloride of Lime, using Kipp's Apparatus. By C. Winkler (*Ber.*, **20**, 184—185).—Dry chloride of lime is intimately mixed with burnt gypsum, and moistened to such a degree that it can only with difficulty be rolled into balls between the fingers. It is made homogeneous by powdering with an iron mortar, and beaten into an iron frame 10 to 12 mm. high by means of an iron mallet. It is then covered with a piece of oil-cloth, and submitted to great pressure. The plate of chloride of lime is then cut into cubes whilst still in the frame, taken out whole, and dried as quickly as possible at 20°. The cubes are then preserved in well-closed vessels. It is used in a Kipp's apparatus with hydrochloric acid (sp. gr. 1·124) diluted with an equal volume of water. The acid must be free from sulphuric acid. N. H. M.

Action of Hydrochloric Acid on Sphalerite. By F. Stolba (*Chem. Centr.*, 1887, 169).—The author has previously recommended the preparation of hydrogen sulphide by the action of hydrochloric

acid on sphalerite (zinc-blende), but further experiments have shown that when using an acid of sp. gr. 1·12, the action stops when about one-half of the acid is decomposed. In spite of this, the method is advantageous, and the residual acid liquid can be used for the evolution of hydrogen or carbonic anhydride. G. H. M.

Constitution of Acids. By W. A. Dixon (*Phil. Mag.*, **21**, 127—130).—Inorganic acids may be supposed to contain displaceable hydrogen, 1st, directly combined with the chlorous element, HCl, &c.; 2nd, combined as hydroxyl, Cl(OH), N(OH), &c.; 3rd, as oxyhydroxyl, $S(OOH)_2$, &c.; or partly in each form $PH(OH)(OOH)$, $P(OH)_2(OOH)$, $S(OH)(OOH)$, $PH_2(OOH)$. Acids of the first kind are usually feeble, and their salts have an alkaline reaction, except when they contain strongly chlorous elements. The group OOH confers high acidity, which is lost when the hydrogen is displaced by an alkaline metal.

Displacement of hydrogen in hydroxyl by an alkaline metal gives salts having an alkaline reaction. When an acid contains both OH and OOH, the hydrogen of the latter group will be first displaced; subsequent displacement of the hydroxylic hydrogen will give a salt having an alkaline reaction.

Silicic acid in solution (obtained by diffusion) may exist as $Si_2(OH)_2(OOH)_2$, instead of $Si(OH)_4$, and hence have an acid reaction. To meet certain cases, special assumptions must be made. Ch. B.

Metals of Ancient Chaldea. By Berthelot (*Compt. rend.*, **104**, 265—271).—The author has examined four tablets found in a stone receptacle under one of the corner stones of the palace of Sargon, which was built 706 B.C. One of the tablets consists of beaten gold, without any notable proportion of any foreign metal; the second consists of silver, almost equally pure, but more or less altered on the surface; the third has undergone considerable alteration, but the internal metallic portion is an alloy of copper and tin, which contains the two metals in the proportions 85·25 : 10·04, and is therefore similar in composition to the majority of ancient bronzes; the fourth consists of pure crystallised magnesium carbonate, a somewhat rare mineral.

A fragment of a vase found during the excavations at Tello was found to consist of pure metallic antimony, and it is evident therefore that this metal was known to the ancients, although it is confounded with lead by Dioscorides, Pliny, and other writers. A small idol from the same excavations had undergone much superficial alteration, but the internal portion was found to consist of pure metallic copper. C. H. B.

Decomposition of Ammonium Chloride by Means of an Alloy of Zinc and Iron. By H. N. Warren (*Chem. News*, **55**, 38—39).—A mixture of dry ammonium chloride and finely powdered zinc, alloyed with 12 per cent. of iron, was put into the right-hand limb of a tube, closed at one end, and bent like the letter N, some mercury or liquid amalgam of tin was put in the lower bend, the open end was

then sealed, and the mixture heated. At the termination of the reaction there was a great pressure of hydrogen, and a considerable quantity of ammonium amalgam in the tube. When the experiment was performed without pressure, or with lime instead of zinc, no ammonium amalgam was obtained. The zinc therefore gives rise to the separation of ammonium, which at first decomposes into ammonia and hydrogen, but as the pressure increases this decomposition no longer takes place, but instead the ammonium is made to amalgamate with the mercury. D. A. L.

Atomic Weights of Silver and Copper. By W. N. Shaw (*Phil. Mag.* [5], **23**, 138—141).—The author determines the amount of copper deposited from a nearly saturated solution of copper sulphate by electric currents of different current density. He finds that the amount reaches a maximum at the highest limit (0·13 ampère) at which a coherent deposit is obtained. For current densities of 0·02—0·0014 ampère the amount multiplied by $1 + \frac{0{\cdot}00002}{d}$, where d is the current density, equals that obtained with high current densities.

From these values the author obtains for the atomic weight of copper the value $63{\cdot}33 = \frac{19 \times 10}{3}$, that of silver being taken as $107{\cdot}66 = \frac{17 \times 19}{3}$, hence $\frac{Ag}{Cu} = \frac{17}{10}$. Taking one-third the weight of the hydrogen-atom as unit, the possible valencies of silver become 1, 17, and 19; of copper, 1, 2, 5, and 19. The only compound known to the author which supports this view is that formed between molten silver and oxygen, which has approximately the composition $AgO_{\frac{1}{18}}$. The author draws attention to the ratio $\frac{17}{10}$ between the atomic weights of potassium and sodium. H. K. T.

Decomposition of Sodium Sulpharsenate with Silver Nitrate. By K. Preis and B. Raymann (*Chem. Centr.*, 1887, 32).—Silver nitrate acts on sodium sulpharsenate in a different manner when added alone, or together with acid, to what it does when the action takes place in ammoniacal solution. In the latter case, silver arsenate and sulphide are almost entirely formed, together with a little arsenite, the quantity of which depends on the amount of free acid present. Since the reaction is instantaneous, the formation of the arsenite is perhaps due to reduction. The authors suggest the following explanation of its formation:—Arsenic acid is a strong acid, whose thermal effect is equal to that of the strongest acids, whilst on the contrary arsenious oxide possesses feeble acidic properties, and even under certain conditions exhibits basic properties. Therefore if the reaction takes place in presence of ammonia, arsenic acid is formed, whilst in the presence of free acid the feebly basic arsenious trioxide is formed. This theory corresponds with the decomposition of silver nitrate by arseniuretted hydrogen; on passing this gas through

neutral silver nitrate solution, arsenious acid goes into solution, whilst if the silver solution is ammoniacal arsenic acid is formed.

G. H. M.

Tetracalcium Phosphate and the Phosphoric Acid of Basic Slag. By H. Otto (*Chem. Zeit.*, **11**, 255—256).—The author's results confirm those of some other investigators; he finds the crystals separated from basic slag consist of tetracalcium phosphate, and moreover, that the phosphoric acid in the basic slag itself behaves with numerous solvents in the same way as tetracalcium phosphate; with alkaline ammonium citrate, however, this is not the case, owing to the interference of the silica and magnesia present in the slag.

D. A. L.

Properties of some Metals. By V. Meyer (*Ber.*, **20**, 497—500).—Magnesium melts at a temperature above the melting point of sodium bromide, melting at 700°, and slightly below that of anhydrous sodium hydroxide, melting at 800°. Experiments made with the object of determining the vapour-density of the metal have failed, inasmuch as it is impossible to volatilise magnesium at an incipient white heat in a neutral gas, such as hydrogen or carbonic oxide; combination of the elements ensues if nitrogen is employed, whilst carbonic anhydride is reduced to carbon by the metal at this temperature. Porcelain is strongly attacked by magnesium at an incipient white heat.

Germanium does not attack porcelain at about 1350°, but is only volatile to a small degree when heated either in hydrogen or nitrogen at this temperature; its vapour-density, therefore, cannot yet be determined. Antimony is completely volatilised at 1300°, but not with sufficient rapidity to allow of its vapour-density being determined; further experiments will be made to determine this constant at a higher temperature. The author finds that mercury can be obtained free from metallic impurities by repeated distillation.

W. P. W.

Effect of Hydrochloric Acid on the Solubility of Chlorides. By R. Engel (*Compt. rend.*, **104**, 433—435).—The relation previously found to exist (Abstr., 1886, 505) between the solubility of chlorides and the proportion of hydrochloric acid in the liquid holds good generally, whether the chlorides belong to the same or different families, and whether they crystallise in the anhydrous or hydrated conditions. Experiments with magnesium and calcium chlorides show that in these cases the sum of the equivalents of the chlorides and hydrochloric acid in the liquid remains constant.

The author criticises Jeannel's conclusion (Abstr., 1886, 972), and considers that his results were due to the fact that the proportion of water added was relatively large compared with the quantities of metallic chloride and hydrochloric acid present.

The precipitation of the chlorides cannot be attributed to the combination of the hydrochloric acid with the water. The solubility of different chlorides is very different, and it would be necessary for the hydrochloric acid to combine with a different amount of water in each case. Both the water of crystallisation of the hydrated chlorides,

and the water combined with the hydrochloric acid play the part of solvents; the action is the same both for anhydrous chlorides and for hydrated chlorides calculated to the anhydrous condition.

Similar results have been obtained with nitric acid and nitrates, but with sulphuric acid and sulphates the phenomena are different.

C. H. B.

Pure Zinc, from the Bertha Zinc Company, Pulaski Co., Virginia. By G. B. Bird (*Amer. Chem. J.*, **8**, 431).—By redistilling commercial spelter from a fire-clay retort with iron front, the amount of impurities is reduced with exception of the iron, which is scarcely diminished. H. B.

Analysis of Shot. By H. Hardaway (*Amer. Chem. J.*, **8**, 432).—Several commercial brands of bird-shot were analysed, especially for arsenic; the amount found, namely, 0·4—3·0 part per 1,000, proved to be less than that usually stated (3 to 8 or 10 parts). H. B.

Preparation of Lead Carbonate. By W. Kubel (*Dingl. polyt. J.*, **262**, 143).—Lead oxide is readily converted into the soluble hydroxide on treatment with a moderately concentrated solution of magnesium acetate. The solution thus obtained has an alkaline reaction, and yields lead carbonate when treated with carbonic anhydride. The white precipitate is collected, washed, and dried, and the solution of magnesium acetate concentrated and used for another operation. D. B.

Action of Lead Oxide on Soluble Chlorides. By G. André (*Compt. rend.*, **104**, 359—360).—If a concentrated solution of calcium chloride is boiled with an excess of lead oxide, care being taken to prevent evaporation, and the liquid is filtered, the filtrate deposits an abundant precipitate, which after washing with alcohol and drying has the composition $CaCl_2,CaO,2PbO + 4H_2O$. When boiled with water it becomes yellow. If the water is left out of account this compound may be regarded as crystallised calcium oxychloride in which 2 mols. of calcium oxide have been replaced by 2 mols. of lead oxide. When the mother-liquor, which is slightly alkaline, is poured into a large excess of cold water, the compound $PbCl_2,3PbO + 3H_2O$ is obtained as an amorphous white precipitate.

A solution of barium chloride when treated in a similar manner yields small slender needles which seem to be a compound of barium chloride with lead oxychloride, but they are decomposed immediately by water and yield lead oxychloride.

Strontium chloride yields small, distinct, brilliant crystals which when washed with alcohol and dried have the composition $SnCl_2,2PbO,5H_2O$. If the mother-liquor is poured into excess of water the compound $PbCl_2,3PbO,3H_2O$ is precipitated.

Lead oxide is dissolved by either a hot or a cold solution of magnesium chloride, but the filtered liquid deposits no precipitate, and only a very slight precipitate is obtained when the solution is poured into an excess of water. C. H. B.

Analysis of a Copper Slag of Bright Red Colour. By N. A. Berry (*Amer. Chem. J.*, **8**, 429—430).—The slag is hard, breaks with conchoidal fracture, and contains small cavities and very minute metallic beads. Treated with hydrochloric and nitric acids, 30·23 per cent. dissolved (27·05 per cent. cuprous oxide), and there remained a yellow powder containing $Cu_2O = 8·64$; $FeO = 11·69$; $SiO_2 = 49·24$. H. B.

Composition of Mirror Amalgam. By G. Harrison (*Amer. Chem. J.*, **8**, 430—431).—The amalgam from a German mirror was found to contain tin 83·78 per cent., mercury 16·60 per cent.

H. B.

Mercurous Hydroxide. By G. B. Bird (*Amer. Chem. J.*, **8**, 426—427; compare Abstr., 1885, 124).—Solutions of mercurous nitrate and of caustic potash in alcohol of 70 per cent., were cooled to −42° and mixed; but little precipitate was formed and that slowly, its colour was a pale amber, changing with rise of temperature into the colours of mixtures of mercurous oxide, mercuric oxide, and finely divided mercury. Judging from the colours of the corresponding lead, copper, and silver compounds, it appears very probable that the pale amber-coloured precipitate obtained was mercurous hydroxide.

H. B.

Action of Mercuric Oxide on Dissolved Chlorides. By G. André (*Compt. rend.*, **104**, 431—433).—Klinger has described a compound, $CaCl_2,2HgO + 4H_2O$, and this the author has also obtained by the action of mercuric oxide on a solution of calcium chloride. The mother-liquor is not precipitated by cold water. If a solution of mercuric oxide in a boiling and concentrated solution of calcium chloride is poured into a large excess of cold water, a brick-red precipitate is obtained which when dried at 100° has the composition $HgCl_2,3HgO$. It is analogous to and possibly identical with the oxychloride obtained by Millon by mixing equal volumes of cold saturated solutions of mercuric chloride and potassium hydrogen carbonate.

A boiling solution of barium chloride, saturated with yellow mercuric oxide and allowed to cool, deposits needles of the compound $BaCl_2,HgO + 6H_2O$, analogous to the barium oxychloride previously described. When treated with water, it becomes yellow. It loses nearly 5 mols. H_2O at 100° and the rest at 150°. If heated in a tube, it gives off water, becoming yellow and finally white. Red mercuric oxide gives the same compound, which, when decomposed by water, yields the red oxide. If the mother-liquor of the oxychloride is poured into cold water, only a slight precipitate is formed.

Strontium chloride solution under similar conditions yields the compound $SrCl_2,HgO + 6H_2O$ in long, slender needles, which lose 3·5 mols. H_2O at 100° and the rest at 130°. It is analogous to strontium oxychloride but contains 3 additional mols. H_2O. Only a slight precipitate is formed when the mother-liquor is poured into cold water.

A cold saturated solution of magnesium chloride dissolves yellow mercuric oxide when heated, but the liquid deposits no compound on

cooling. If poured into a large excess of water, it yields a white amorphous precipitate of the composition $2HgCl_2,3HgO$.

The general results show that these mixed compounds are true oxychlorides which are sometimes strictly analogous to the simple oxychlorides, whilst sometimes their composition is not exactly similar. Both classes of compounds agree in their alterability in contact with water. C. H. B.

Basic Aluminium Sulphate. By K. J. Bayer (*Chem. Zeit.*, **11**, 38; 97—98).—A basic aluminium sulphate, $3Al_2O_3,2SO_3 + 9H_2O$, is produced when excess of aluminium hydroxide, prepared by precipitation by means of carbonic anhydride, is boiled for some time with sulphuric acid. This basic sulphate is practically insoluble in sulphuric or hydrochloric acid, for even on prolonged digestion with sulphuric acid, sp. gr. 1·3—1·4, only part of it passes gradually into solution. It is, however, completely soluble in aqueous soda. At 100°, or over sulphuric acid, it does not lose water, but when heated to low redness it loses 9 mols. H_2O without further decomposition, whilst at a bright red heat it decomposes with evolution of sulphurous anhydride. The slightly ignited and anhydrous salt yields a basic sulphate to water which is precipitated on boiling. When the basic sulphate described above exists in aluminium sulphate, it is a sure sign that the latter has been prepared by the alkaline process. D. A. L.

Fluorine and Manganese Compounds. By O. T. Christensen (*J. pr. Chem.*, **35**, 161—181; compare this vol., p. 335).—*Chromium potassium fluoride*, $6KF,Cr_2F_6$, is obtained by fusing chromic hydroxide with an excess of potassium hydrogen fluoride and extracting the residue in the cold with water containing hydrogen fluoride; it is a green, crystalline powder practically insoluble in water, and yields insoluble chrome alum on evaporation with concentrated sulphuric acid. The compound $4KF,Cr_2F_6 + 2H_2O$, prepared by mixing solutions of its constituents, is a green salt very sparingly soluble in water, but soluble in hydrochloric acid.

Iron potassium fluoride, $4KF,Fe_2F_6 + 2H_2O$, is prepared by fusing ferric hydroxide with an excess of potassium hydrogen fluoride; it is a white, crystalline powder, very sparingly soluble in water, and the solution gives no reaction with potassium thiocyanate. This salt is probably identical with that described by Nicklès containing 1 mol. H_2O (*J. Pharm.* [4], **7**, 15).

Manganese ammonium fluoride, $4NH_4F,Mn_2F_6$, is obtained by mixing a solution of manganosomanganic oxide in hydrofluoric acid with one of ammonium fluoride, ether as a red, crystalline salt, or in dark, prismatic crystals, and is sparingly soluble in water containing hydrogen fluoride. The *sodium* salt, $4NaF,Mn_2F_6$, is a red, crystalline powder, consisting of microscopic, rectangular tables; the *silver* salt, $2AgF,Mn_2F_6 + 8H_2O$, forms dark, almost black crystals, and loses the greater part of its water of crystallisation at 100°, the remainder at 110°. When manganese fluoride is added to a solution of chloropurpureocobalt carbonate in hydrofluoric acid, chloropur-

pureocobalt manganese fluoride is obtained as a lustrous, crystalline precipitate consisting of microscopic rectangular tables.

Berzelius has shown that when aluminium hydroxide is boiled with a solution of sodium fluoride, cryolite is formed, and Schuch has pointed out that aluminium hydroxide is obtained when cryolite is boiled with sodium hydroxide; the author has endeavoured to find out the conditions of equilibrium for these changes, and proves that there is a definite limit to the first reaction, but not to the second, owing to the fact that the separated sodium fluoride encloses unaltered cryolite and protects it from further action. Sodium fluoride solution is not decomposed when boiled with ferric, chromic, or manganic hydroxides. The author considers the double fluorides and double cyanides of the iron-aluminium-group to be analogous in constitution.

W. P. W.

Solubility of Manganese Sulphide in Fused Potassium Sulphide. By E. Claassen (*Amer. Chem. J.*, **8**, 436—437).—When fusing magnetite with soda and sulphur for the purpose of detecting vanadium, it was found that a considerable amount of manganese was also extracted from the fused mass by treatment with water.

H. B.

Preparation of Ammonium Dichromate. By J. J. Hood (*Chem. Zeit.*, **11**, 55).—Chrome-iron ore is heated with sodium or potassium salts, the resulting monochromate is dissolved in water, treated with 2 equivalents of acid, and then neutralised with ammonia or ammonium carbonate. The solution containing a dichromate and a sulphate, chloride, or nitrate, as the case may be, is concentrated, the latter salts as they crystallise are removed, and finally on cooling ammonium dichromate crystallises out. The potassium or sodium salts are used again for heating with fresh chrome-iron ore.

D. A. L.

Extraction of Vanadium and Chromium from Iron Ores, particularly from Magnetite. By E. Claassen (*Amer. Chem. J.*, **8**, 437—443; comp. Abstr., 1886, 428).—It is impossible to obtain in a soluble form all the vanadium and chromium contained in certain ores (especially hard dense ores like magnetite), by fusion with sodium carbonate and nitre or sulphur. The finely powdered ore, if treated with water (1 part) and sulphuric acid (2 parts), and then gradually heated until all sulphates are decomposed, is converted into the finest possible powder, and from this the vanadium and chromium may be completely extracted by a single fusion. If only vanadium is to be estimated, the following is the better method of procedure, as a solution free from chromium is at once obtained. The powder left after treatment with sulphuric acid is fused with three parts of soda and three of sulphur, the melt extracted with water, the filtrate containing a thiovanadate boiled with dilute nitric acid, and the precipitated vanadium sulphide collected, dried, and excess of sulphur removed by treatment with carbon bisulphide; the filtrate, which always contains some vanadium, is evaporated to dryness, mixed with the precipitated sulphide, and fused with a little soda. The fused mass is extracted with water, and the filtrate which

contains a vanadate and also nitrites, is made neutral by continued boiling with small quantities of ammonium nitrate, and precipitated by lead nitrate. The washed lead vanadate is digested with hydrochloric acid and alcohol, and the lead chloride removed by filtration and washing with alcohol; the alcoholic filtrates are evaporated, redissolved in water, and the last trace of lead removed by hydrogen sulphide; the filtrate when evaporated and ignited leaves impure vanadium pentoxide; it is oxidised by ignition with ammonium nitrate, extracted with ammonia, and finally obtained pure by evaporation and ignition.

If both vanadium and chromium are to be estimated, the following method may be substituted, both being extracted together from the ore and then separated afterwards. The ore after the treatment with sulphuric acid is fused with thrice its weight each of soda and nitre, and the soluble portion dissolved out by water. The solution is made neutral by boiling with ammonium nitrate, then precipitated by lead acetate, and the lead removed as before described. The dried residue containing chromium and vanadium is fused with three parts of soda and three of sulphur, and the mass extracted with water. The filtrate containing the vanadium is treated as before; the residue containing the chromium is fused with alkali and nitre, and precipitated as usual as lead chromate. H. B.

Gold. By G. Krüss (*Annalen*, **237**, 274—307; compare this vol., pp. 15, 340).—Only three oxides of gold exist, namely: Au_2O, Au_2O,Au_2O_3, and Au_2O_3. These oxides have been previously described by the author (*loc. cit.*).

Oberkampf (*Ann. Chim.*, **80**, 140), Figuier (*Ann. Chim. Phys.* [3], **11**, 336), Buisson (*J. Pharm.*, **16**, 629), and Russell (this Journ., 1874, 11) state that gold is precipitated by hydrogen from a solution of auric chloride. This is denied by Proust (*J. Phys.*, **62**, 131) and Schweigger-Seidel (*Schweigger's Journ.*, **65**, 268). The author finds that hydrogen which has been purified by passing through solutions of sodium hydroxide, silver nitrate, potassium permanganate, and over red-hot copper, has no action on auric chloride.

The discrepancies between the author's results and Raschig's (this vol., p. 112) arise from two sources. Aurous oxide prepared by the action of mercurous nitrate on auric chloride contains mercury. The formula $Au_2O + 2H_2O$, which Raschig obtained for the oxide dried over phosphoric anhydride, is consequently incorrect.

Auric oxide and auric chloride are not reduced by pure sodium hydroxide. If the sodium hydroxide contains organic matter, oxides of gold are precipitated, but auric acid is not formed.

W. C. W.

Formation of Platinum Silicide. By F. P. Miles (*Amer. Chem. J.*, **8**, 428; compare Abstr., 1886, 124).—The conditions under which platinum silicide was formed, are found to be the presence of reducing gases such as carbonic oxide, of silicon tetrafluoride, and of a basic substance such as magnesia. H. B.

Mineralogical Chemistry.

Composition of the Black Zinc Blende of Freiberg. By A. Stelzner and A. Schertel (*Chem. Centr.*, 1887, **92**).—The analysis of black blende from five different veins in the Freiburg district gave the following numbers:—Zn, 49·83—51·73; Fe, 11·97—13·44; S, 32·51—33·69; Mn, 0·08—0·83; Cd, 0·19—0·42; Sn, 0·06—0·55; In, traces. The tin is present as sulphide; the ratio of zinc to iron is nearly 3·3 : 1. The mechanical impurities were small quantities of tinstone and quartz. Both these impurities, amounting to 0·6—1·0 per cent., were present in blende from 10 different localities.

The tinstone belongs to the type of needle-tinstone, and forms columnar, often twinned crystals, about 0·8 mm. long, which are often embedded in the blende, and often in the quartz. The latter is in the form of small, irregular crystals of the combination P∞P, and sometimes encloses blende. The formation of zinc-blende, tinstone, and quartz, must, therefore, generally have taken place simultaneously in the Freiburg district. G. H. M.

Quartzite. By P. Holland (*Chem. News*, **55**, 49—50).—The specimen examined was taken from stone quarries at Nill's Hill, Pontesbury. A detailed description and a figure of its appearance under the microscope are given; it proved to be a compact felspathic quartzite. The analytical numbers obtained from it were as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	K_2O.	Na_2O.	Carbon.	Combined water.
94·85	2·38	0·62	0·67	0·71	0·07	0·63

In some darker-coloured fragments the carbon amounted to 0·13 per cent. D. A. L.

Plattnerite. By E. Kinch (*Min. Mag.*, **7**, 63—64).—A mineral from Leadhills, Lanarkshire, analysed by the author, proved to be plattnerite, a mineral not examined since it was first noticed by Breithaupt and Plattner in 1837. The following are the analytical results obtained:—

Loss on ignition.	PbO.	Total.
7·10	92·66	99·76

It is a black mineral in globulous concretions with crystalline exterior. The hardness is about 5. The sp. gr. is 8·54, or somewhat lower than that given by Breithaupt. B. H. B.

New Variety of Dufrenite from Cornwall. By E. Kinch, F. H. Butler, and H. A. Miers (*Min. Mag.*, **7**, 65—70).—The authors have examined examples of crystallised mineral from East Cornwall, presenting features dissimilar from those of any known species, but presumably referable to dufrenite. The unaltered crystals have a

vitreous lustre, and vary in colour from black to apple-green. The crystals occur in the form of rectangular tables, 1 to 2 mm. square and $\frac{3}{4}$ mm. thick. They may be regarded as orthorhombic plates formed by the micropinacoid faces, bevelled at the sides by small faces of the prism, and bounded at the top and bottom by the basal planes. The crystallographic characters agree very closely with those of dufrenite from Waldgirmes, described by A. Streng (Abstr., 1881, 527). The green crystals have a hardness of 4·5, and a sp. gr. of 3·233. Analysis gave the following results:—

H_2O.	SiO_2.	CuO.	P_2O_5.	Fe_2O_3.	CaO.	MgO.	Total.
10·62	0·53	0·95	30·26	55·63	1·50	trace	99·49

These results are compared with the various published analyses of dufrenite, and the authors conclude that the mineral described, as well as other varieties described under the head of dufrenite, contains a larger proportion of phosphoric acid to base than is compatible with the usual formula for dufrenite, $2Fe_2O_3,P_2O_5,3H_2O$. The species should, therefore, be divided into two, one having the formula $5Fe_2O_3,P_2O_5,8H_2O$, or possibly, in some cases, less water.

B. H. B.

Talc used in Paper-making. By W. I. Macadam (*Min. Mag.*, **7**, 75).—This mineral, known in commerce as *agalite*, is obtained from New Jersey. It is largely used for paper-making in place of kaolin, and gives a much purer effluent. The high glaze of American paper is largely due to the use of this mineral. It is of a highly fibrous character, insoluble in water, and greasy to the touch. In colour, it is almost pure white. Its sp. gr. varies from 2·22 to 2·562. Analysis gave the following results:—

SiO_2.	MgO.	FeO.	Al_2O_3.	H_2O.	Loss.	Total.
62·08	33·13	0·10	0·31	4·29	0·09	100·00

B. H. B.

Phenacite from Colorado. By S. L. Penfield (*Amer. J. Sci.*, **33**, 130—134).—The occurrence of phenacite in the United States was first mentioned by Cross and Hillebrand (Abstr., 1883, 1065). Crystallographical descriptions of the phenacite from Florissant have also been published by Hidden (Abstr., 1885, 878; and 1887, 118). The crystals occur at Topaz Butte, near Florissant, and about 16 miles from Pike's Peak. They are remarkably similar to those described by N. v. Kokscharoff from the Ural. The planes observed are of especial interest as belonging to the rhombohedral-tetartohedral division of the hexagonal system.

The author also describes some remarkable crystals from a new locality, Mt. Antero, in Chaffee Co. They are terminated mainly by rhombohedra of the third order. B. H. B.

The Crystal Beds of Topaz Butte. By W. B. Smith (*Amer. J. Sci.*, **33**, 134—135).—The *crystal beds* from which most of the specimens labelled *Pike's Peak* have actually come are situate 20 miles north-west of that point. Topaz Butte, a point 5 miles north of Florissant, marks the southern limit of the beds. The largest phena-

cite ever found in this locality is a lenticular crystal, 15 mm. in diameter.

A few phenacite crystals have been observed in the interior of smoky quartz and amazon-stone crystals: these minerals showing no evidence of secondary growth. Phenacites have also been found half in quartz and half in amazon-stone, when the two minerals are in contact. B. H. B.

Topaz from the Thomas Range, Utah. By A. N. Alling (*Amer. J. Sci.*, **33**, 146).—The topaz crystals examined were found in the Thomas Range, 40 miles north of Sevier Lake, where they occur in rhyolite (compare W. Cross, Abstr., 1886, 991). They vary from 3 to 10 mm. in length, and are perfectly colourless. The planes observed were $\infty\breve{P}\infty$, 0P, ∞P, $\infty\breve{P}2$, $2\breve{P}\infty$, $2\breve{P}\infty$, $4\breve{P}\infty$, $\frac{2}{3}$P, P, 2P, 4P. The axial ratio was calculated to be

$$a : b : c = 0{\cdot}5285 : 1 : 0{\cdot}47715,$$

values approximating very closely to those obtained by v. Kokscharoff for the Siberian crystals, but varying very widely from the axial ratios for crystals from Ehrenfriedersdorf, Altenberg, Schneckenstein, and Brazil. B. H. B.

Occurrence of Strontia in Heulandite. By P. Jannasch (*Ber.*, **20**, 346—349).—The following analyses of heulandite from different localities are given:—

	Andreasberg.	Farsathal.		Teigashorn.
SiO_2	56·11	60·07	57·71	58·43
Al_2O_3	17·15	14·75	16·42	16·44
Fe_2O_3	trace	0·62	—	—
CaO	4·26	4·89	6·96	7·00
SrO	3·63	1·60	0·54	0·35
MgO	trace	—	—	—
Na_2O	3·31	2·36	1·49	1·40
K_2O	0·27	0·44	0·35	0·21
Li_2O	trace	trace	trace	trace
H_2O	16·28	15·89	16·50	16·45

The formula of heulandite would therefore be

$$H_4(Ca,Sr,Na_2,K_2)Al_2(SiO_3)_6 + 3\tfrac{1}{2}H_2O \text{ or } 4H_2O.$$

In order to separate the calcium from the strontium, they are precipitated from the weak ammoniacal solution as oxalates, the precipitate redissolved and again precipitated. The ignited mixture of earths is converted into nitrates, and separated by means of alcohol and ether. The undissolved strontium salt is then dissolved in hot water, precipitated with dilute sulphuric acid in presence of alcohol, and weighed as sulphate. N. H. M.

Sodium Felspar from Krageroe, Norway. By Bischof (*Chem. Centr.*, 1887, 169—170).—This is of a brownish colour without any

distinct foreign markings, and with fine mother-of-pearl-like laminations. Dried at 100°, its composition is—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
65·35	21·66	0·64	1·79	0·16	0·52	9·88	0·25

showing that it is a sodium felspar containing a noteworthy amount of lime. It melts more easily than the potassium felspar from Norway.

G. H. M.

Occurrence of Silver in Volcanic Ash from the Eruption of Cotopaxi, July 22nd—23rd, 1885. By J. W. Mallet (*Chem. News*, 55, 17).—The sample was collected at Bahia de Caraguez, where ash had fallen to the depth of several inches although the place is 120 miles to the westward of Cotopaxi. The specimen consisted of a very fine, mobile powder soft to the touch and of a light brownish-grey colour. Under the microscope it appeared to consist of minute, more or less sharp or splintery-edged granules and spicules; quartz, a white and pink or reddish felspar, augite, magnetite (strongly magnetic), and thin scales of deep red specular iron oxide were easily distinguished. When strongly heated, the ash turned dark red-brown, and fused to a nearly black slag. Its sp. gr. = 2·624 at 18°; 0·21 per cent. of the ash was soluble in boiling water and 6·94 per cent. was dissolved by hydrochloric acid from the portion insoluble in water. The ash dried at 100° contained per cent.—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.
56·89	19·72	4·06	3·65	1·91	5·87	5·14	1·96	0·62

with traces of TiO_2, MnO, Li_2O, Ag, Cl, SO_3, P_2O_5.

The silver present amounted to about 1 part in 83,600 of ash, but although the proportion is so small the total amount ejected during the eruption would be considerable when the vastness of the mass of volcanic ash is taken into consideration. The silver was probably present as chloride. This is the first time silver has been found in volcanic ash.

D. A. L.

Diabase Porphyrite from the Neighbourhood of Petrosawodsk. By C. v. Vogdt (*Chem. Centr.*, 1887, 200).—The masses of rock running through the diluvium in the form of *roches moutonnées* belong partly to forms rich in augite and partly to forms rich in felspar. Only the latter were submitted to further examination. The porphyritic felspar occurs as orthoclase frequently mixed with oligoclase and labradorite and entirely converted into radial aggregates; whilst the ground-mass, which is rich in epidote, appears to consist chiefly of an albitic felspar. The augite is very chloritic.

G. H. M.

Meteoric Iron from Augusta Co., Virginia. By G. F. Kunz (*Amer. J. Sci.*, 33, 58—59).—This mass of meteoric iron was found near the place where the largest of the three masses from Augusta Co., described by Mallet (Abstr., 1871, 1020), was found. Its present dimensions are 8·5 cm. by 6·5 cm., 7 cm. at the wider end and 3 cm. at the smaller end. The following is an analysis of the mass:—

Fe.	Ni.	Co.	Cu.	Sn.	P.	S.
90·293	8·848	0·486	0·016	0·005	0·243	0·012

C.	Si.	Total.
0·177	0·092	100·072

with traces of manganese, chromium, and chlorine. B. H. B.

Coahuila Meteorites. By O. W. Huntington (*Amer. J. Sci.*, **33**, 115—118).—The author shows that the assumed new meteorite found near Fort Duncan, Maverick Co., Texas, and described by W. E. Hidden (this vol., p. 119), belongs to the same fall as the meteorites described by J. L. Smith under the head of Coahuila irons, and supposed to belong to one fall. The irons referred to are, the Santa Rosa Sancha Estate iron, found in 1850; the Butcher iron, found in 1866; the San Gregorio iron; and the Chihuahua Hacienda de Conception iron. B. H. B.

Supposed Metallic Meteorite from Highland Co., Virginia. By F. P. Miles (*Amer. Chem. J.*, **8**, 427—428).—The metal contains Fe = 99·716, P = 0·106, C = 0·032, S = 0·058, but nickel and cobalt are absent. It is probably a relic from an early bloomery fire, although there are no records of such in the neighbourhood. H. B.

Analysis of the Water from an Artesian Well in the Tunisian Chotts, and from the Spring at Oued Ref. By De Lesseps (*Compt. rend.*, **104**, 272).

	$CaCO_3$.	$MgCO_3$.	$CaSO_4$.	$MgSO_4$.	Na_2SO_4.
Artesian well.....	0·607	none	1·196	0·490	none
Spring at Oued Ref	0·252	0·185	1·027	none	1·582

	NaCl.	KCl.	$MgCl_2$.	Residue per litre.
Artesian well.....	0·052	none	0·842	3·187
Spring at Oued Ref	1·205	0·061	none	3·412

C. H. B.

Water from the Wells of Zemzem. By P. v. Romburgh (*Rec. Trav. Chem.*, **5**, 565—273).—The waters from the wells of Zemzem, or Hagar's Wells, near Mecca, have been celebrated for centuries past as holy to Mussulmans and as possessing therapeutic value; it is even probable that to them the town of Mecca owes its origin. For some time, the water supply was taken from the wells, but as this was regarded as sacrilege, other sources were subsequently used. It appears that as the supply of water is almost inexhaustible, it arises from one stream flowing underground; there is, however, reason to believe that it is being contaminated by the sewage of Mecca. The results of analysis in gram per litre are as follows:—

Cl.	SO_3.	N_2O_5.	CO_2.	SiO_2.	CaO.	MgO.
0·5563	0·3955	0·7255	0·317	0·0472	0·412	0·152

Na_2O.	K_2O.	P_2O_5.
0·5776	0·2719	trace

The sp. gr. at 18° was 1·0025. A bacteriological examination of the water gave no particular results. P. Frankland in 1881 made an analysis of a sample of water from Hagar's Well; the results, however, were different from those given above; either the water undergoes considerable changes or, more probably, the two samples were not taken from the same source. V. H. V.

Organic Chemistry.

Vaselin. By C. Engler and M. Boehm (*Dingl. polyt. J.*, **262**, 468—475 and 524—530).—The authors call vaselin the substance extracted from petroleum residues, whilst the mixture of heavy mineral oil (*Paraffinum liquidum*) with ceresine (*Paraffinum solidum*) is regarded as "artificial vaselin." For the preparation of the natural product, two Galician oils were used. Both oils were highly dichroïc, had a green colour by reflected light and a colour varying from yellowish to brownish-red by transmitted light, and exhibited the following properties when subjected to distillation.

		Fraction below 150°.		150° to 200°.	
	Sp. gr. at 15°.	per cent. by vol.	per cent. by weight.	per cent. by vol.	per cent. by weight.
Oil I..	0·812	30·2	26·7	35·9	35·5
„ II..	0·820	21·8	20·0	51·7	51·2

	290° to 340°.		Above 340°.	
	per cent. by vol.	per cent. by weight.	per cent. by vol.	per cent. by weight.
Oil I	5·3	6·5	27·7	31·1
„ II	8·8	9·4	17·0	18·9

For the production of vaselin from these oils, two methods were employed, the first consisting in dissolving the residues in petroleum spirit, bleaching the solution by filtration through animal charcoal, and expelling the solvent by distillation with steam, whilst the second method involved bleaching the oil and subjecting it to distillation in a vacuum (mercury column = 10—15 mm.) to 250°. The product obtained according to the first process formed a colourless, translucent pasty mass melting at 32° and exhibiting no crystalline structure, even on application of cold. The vaselin extracted from the bleached oils was colourless, translucent, and free from odour. It had the following properties:—

	Yield.	Sp. gr.	Melting point.
Oil I	13·8	0·8809	30—31°
„ II	13·2	0·8785	30—31

The composition of the different vaselins is illustrated in the subjoined table.

	From residues.		From Petroleum Oil I.			From Petroleum Oil II.	
C	86·99	86·67	86·30	86·54	86·55	86·14	86·17
H	13·14	13·15	13·99	13·73	13·74	13·50	13·72

These results show that vaselin is composed exclusively of hydrocarbons. The oils obtained by subjecting the bleached petroleum to fractional distillation were also found to contain only carbon and hydrogen, both oxygen and sulphur being absent. The bleaching process appears to remove all oxygenated constituents and increase the amount of saturated hydrocarbons, the charcoal retaining the less highly hydrogenised hydrocarbons. Attempts were made to increase the melting point of vaselin by subjecting it to partial redistillation. It was not, however, possible to raise the melting point more than two or three degrees, whilst prolonged distillation resulted in reducing the melting point, probably owing to decomposition of the vaselin. By dissolving vaselin in ether and subjecting the ethereal solution to fractional precipitation with alcohol, the authors succeeded in separating a solid and liquid substance from vaselin. 100 grams gave 40·8 grams of solid vaselin of 0·8836 sp. gr., melting at 40°, and 59·2 grams of liquid vaselin of 0·8809 sp. gr., solidifying at −10°. Both products had the same constitution, and approximately the same boiling points. American vaselin melting at 32—33° yielded 14 per cent. of solid vaselin melting at 49—50° and 86 per cent. of liquid vaselin. It is possible to separate "artificial vaselin" into a solid and liquid substance, but the chemical and physical properties of the component parts are essentially different. D. B.

Piperilene. By G. Magnanimi (*Gazzetta*, **16**, 390—392).—Piperilene, C_5H_8, on bromination, forms two isomeric tetrabromo-compounds, $C_5H_8Br_4$, the one identical with a substance previously described by Hofmann, melting at 114·9°, the other, a colourless liquid boiling at 115—118° under a pressure of 4 mm., and exhibiting no signs of solidification when subjected to a freezing mixture.

Attempts were made to determine the molecular weight of the solid tetrabromo-compound by means of the lowering of freezing point of benzene caused by the solution therein of this substance, according to the methods proposed by Raoult and by Paternò and Nasini; the results indicated that the compound was not a polymeric modification of the liquid substance above described. V. H. V.

Hydrogenation of Propionitrile. By G. Pisanello (*Gazzetta*, **16**, 446—448).—It has recently been shown by Spica that the nitriles on hydrogenation yield, besides the corresponding primary amines, small quantities of the secondary and tertiary amines. It is here shown that propionitrile, on hydrogenation with tin and hydrochloric acid, yields besides propylamine, small quantities of di- and tri-propylamine, as evidenced by fractional crystallisation of their platino-

chlorides, and determination of the platinum therein; the formation of the secondary amines was also proved by Liebermann's colour reaction. V. H. V.

Etherification by Double Decomposition. New Ethereal Salts of Nitrous Acid. By G. Bertoni (*Chem. Centr.*, 1887, 35—36; compare Abstracts, 1886, 217 and 975).—*Tertiary amyl nitrite*, $C_5H_{11}\cdot O\cdot NO$, is prepared by shaking together at the ordinary temperature tertiary amyl alcohol (3 mols.) with glyceryl trinitrite (1 mol.), and occasionally adding a lump of ice. The liquid separates into two layers, the upper of which is the ethereal salt. This is washed with very dilute aqueous soda, then with water, finally dried over fused calcium nitrate, and fractionally distilled. It is a mobile, slightly yellow, pleasant smelling liquid, boiling at 92—93°, sp. gr. at 0° = 0·9033, very slightly soluble in water, easily soluble in amyl alcohol, ether, chloroform, benzene, &c., decomposed by methyl and ethyl alcohol with formation of methyl and ethyl nitrites. When inspired, it does not give the same symptoms as ordinary amyl nitrite. It is violently decomposed by strong sulphuric acid, and reduced by ammonium sulphide and hydrogen sulphide, with separation of sulphur; it is saponified by alkalis.

α-Propylene dinitrite, $ON\cdot O\cdot CH_2\cdot CHMe\cdot O\cdot NO$, is prepared in the same way as the preceding compound by heating a mixture of α-propylene glycol and glyceryl trinitrite on the water-bath. It is a yellowish, very mobile liquid, of suffocating odour, boiling at 108—110°, sp. gr. at 0° = 1·144, insoluble in water, soluble in ether, chloroform, benzene, &c., slowly decomposed by water, quickly by methyl and ethyl alcohol, it is dissolved by cold and decomposed by hot acetic acid; dilute sulphuric acid decomposes it. When exposed to sunlight in a closed vessel, it explodes violently.

Secondary octyl nitrite, $C_8H_{17}\cdot O\cdot NO$, is prepared by treating secondary octyl alcohol (3 mols.) with glyceryl trinitrite (1 mol.) at the ordinary temperature, and proceeding as above. It is a dark yellow, mobile liquid, boiling at 165—166°, sp. gr. at 0° = 0·881, insoluble in water, soluble in the alcohols, and decomposed by the lower members, also soluble in ether, chloroform, benzene, &c. When acted on by acids, it is decomposed in the same way as the preceding compounds.

The author finds that the physiological actions of these nitrites and also of allyl nitrite (Abstr., 1886, 218) is not different from that of other ethereal nitrites. The poisonous properties of these nitrites increase on the one hand with the percentage of NO_2, and on the other with their decomposibility; they stand in the following order: α-propylene, allyl, tertiary amyl, secondary octyl nitrite.

G. H. M.

Phosphoplatinous Chloride. By E. Pomey (*Compt. rend.*, **104**, 364).—Phosphoplatinous chloride dissolves readily in propyl alcohol, with subsequent development of heat and evolution of hydrogen chloride. On adding water to the liquid, a yellow, crystalline precipitate of the compound $P(C_3H_7O)_3PtCl_2$ is obtained. It can be recrystallised from alcohol. C. H. B.

Formose. By O. Loew (*Ber.*, **20**, 141—144).—The author discusses the properties of formose and its analogy with levulose, and considers it to be a sugar (compare Tollens, *Ber.*, **19**, 2134).

Reaction for Fruit-sugar. By T. Seliwanoff (*Ber.*, **20**, 181—182).—A cold aqueous solution of cane-sugar (2 parts) and resorcinol (1 part) is treated with concentrated hydrochloric acid and quickly warmed. The mixture becomes red, and deposits on cooling an abundant dark precipitate. The latter is amorphous, and is soluble in alcohol. Fruit-sugar and raffinose give the reaction. Dextrose, galactose, maltose, milk-sugar, and inosite gave no coloration.

Levulinic acid gives Baeyer's aldehyde reaction with phenol. On adding an alkali to the alcoholic solution of the red condensation product, it becomes first blue, then green, and finally yellowish-grey. When an alcoholic solution of levulinic acid and resorcinol is treated with fuming hydrochloric acid, and water added, the solution gives a white, resinous precipitate, analogous to those obtained by Michael (Abstr., 1884, 597) by the condensation of aldehydes with resorcinol. It becomes red when exposed to air. Quinones and pyruvic acid give the same reaction (compare also *Chem. Zeit.*, **9**, 231).

N. H. M.

Inosite. By Macquenne (*Compt. rend.*, **104**, 297—299).—Inosite heated at 170° for several hours with 15 times its weight of hydriodic acid of sp. gr. 1·85, yields a small quantity of benzene, together with triidophenol, a result which confirms the constitution previously attributed to inosite (this vol., p. 355). Zinc powder yields no definite products, and sodium amalgam exerts no reducing action.

Chromic acid oxidises inosite in the cold, with formation of formic acid and evolutiou of some carbonic anhydride. Potassium permanganate in neutral or alkaline solution oxidises it to carbonic anhydride. The halogens have no action in presence of water in the cold, but bromine and water at 100° yield the brown products previously described (*loc. cit.*).

Boiling dilute nitric acid has no action on inosite, but the concentrated acid attacks it regularly at 100° with formation of oxalic acid, but if the reaction is conducted in an open dish on a water-bath, no oxalic acid is formed, and if the liquid is evaporated to dryness, it leaves a white residue which dissolves in water with effervescence, forming a solution of tetrahydroxyquinone, $C_6O_2(OH)_4$, which may be precipitated in the form of the barium compound $C_6O_2(OH)_2O_2Ba$. In presence of air and a slight excess of alkali, tetrahydroxyquinone rapidly alters to dihydroxydiquinone, a very unstable substance which yields with barium salts an eosin-coloured precipitate, C_6O_6Ba.

If the solution of the products of the action of nitric acid is mixed with an excess of sodium carbonate and a small quantity of alcohol, it deposits a greenish-black crystalline powder, which contains the disodium compounds of tetrahydroxyquinone and dihydroxydiquinone. If this mixture is decomposed by hydrochloric acid, and the product recrystallised from boiling alcohol, it yields tetrahydroxyquinone which may be purified by washing with water. When the tetrahydroxyquinone is treated with cold concentrated nitric acid, heat is

developed, nitrogen oxides are evolved, and the hydrated triquinone, $C_6O_6 + 8H_2O$, described by Nietzki and Benckiser, is obtained as a white crystalline powder; this may be reconverted into tetrahydroxyquinone by suspending it in water, and passing a current of sulphurous anhydride into the liquid. If the triquinone is heated with water it becomes yellow, and if the liquid is evaporated after neutralising with potash, potassium croconate, $C_5O_5K_2 + 2H_2O$, is obtained in beautiful crystals, which are also formed when a current of air is passed into an alkaline solution of tetrahydroxyquinone or rhodizonic acid.

Inosite, in fact, yields the same products of oxidation as those which have been obtained by Nietzki and Benckiser by the oxidation of hexahydroxybenzene, a result which establishes the constitution ascribed to inosite by the author in his previous paper (*loc. cit.*).

C. H. B.

Dry Distillation of Starch with Lime. By V. Horvat (*Chem. Centr.*, 1887, 38—39).—The substances were used in the proportion of 1 : 4. The products found were acetone, mesityl oxide, isophorone, boiling at 207°, and identical with that obtained by heating acetone with lime or soda, and isomeric with the phorone from acetone and hydrochloric acid. The fraction boiling between 128° and 207° consisted of a series of ketones of the formula $C_nH_{2n}O$, and that boiling above 207° of still higher condensation products of acetone than isophorone. The latter did not yield adipic acid when oxidised.

G. H. M.

True Nature of Nägeli's Starch-cellulose. By A. Mayer (*Chem. Centr.*, 1887, 6).—When starch-granules are treated with saliva or dilute acids, delicate skeletons always remain behind, and from Nägeli's researches have hitherto been considered to consist of cellulose. The starch-granule, therefore, appeared to be composed of an intimate mixture of two substances, cellulose, and a substance which Nägeli called granulose. Mayer now states that these skeletons do not consist of a substance which is contained in intact starch-granules, but are really a conversion product formed by the action of the acids or ferment employed, and are identical with amylodextrin. The use of the terms starch-cellulose and granulose must, therefore, be abandoned, and the homogeneous substance of the starch-granule be simply called starch-substance.

G. H. M.

Paragalactin. By E. Schulze and E. Steiger (*Ber.*, **20**, 290—294).—When finely-powdered seeds of *Lupinus luteus*, after removal of the fat by ether, are treated with cold, very dilute aqueous potash, both the constituents soluble in water and the albuminoids are removed; the residue is somewhat gelatinous, and contains in a very impure state the substance which the authors term paragalactin. This substance could not be obtained in a state of purity, as no solvent could be found for it which did not cause alteration. It seems to form 25 per cent. of the seed, and is probably a carbohydrate of the formula $C_6H_{10}O_5$; when heated with dilute acids, it is converted into galactose, no other sugar being formed. It is not dissolved by heating with water under pressure, nor is it converted into a sugar

by diastase. By the action of tartaric acid, or of hot 10 per cent. aqueous potash, solutions are obtained from which, on addition of alcohol, white gelatinous substances separate; these, however, would seem to be decomposition products. An acetyl-derivative prepared from the substance obtained by the last method, gave numbers agreeing with the formula $C_6H_7O_5Ac_3$, and began to decompose at 225° without previous fusion. A. J. G.

Trimethylpropylammonium Iodide and Hydroxide. By T. Langeli (*Gazzetta*, **16**, 385—389).—When propylamine and methyl iodide, preferably diluted with alcohol, are heated together, trimethylpropylammonium iodide is formed, together with propylmethylamine and propylamine hydroiodides, thus: $4PrNH_2 + 4MeI = PrMe_3NI + NHPrMe,HI + 2NH_2Pr,HI$. The first of these salts crystallises in long needles melting at 190°; the corresponding chloride forms a crystalline mass, and the platinochloride, $(NMe_3Pr)_2,PtCl_6$, a yellow crystalline precipitate. Trimethylpropylammmonium hydroxide decomposes on distillation into propylene and trimethylamine, thus: $CH_2Me{\cdot}CH_2{\cdot}NMe_3{\cdot}OH = CH(CH_3) : CH_2 + NMe_3 + OH_2$. V. H. V.

Salts of Diisobutylamine and Triisobutylamine. By H. Malbot (*Compt. rend.*, **104**, 366—369).—*Diisobutyl hydrochloride*, $N(C_4H_9)_2H,HCl$, is easily obtained in a state of purity, and forms plates or leaflets with a greasy lustre, the transparence and aggregation of the crystals depending on the nature of the solvent. It is somewhat easily soluble in alcohol and in water, slightly soluble in isobutyl alcohol, and only very slightly soluble in ether. It sublimes somewhat rapidly at 240°, and if maintained for some time at 262° it melts partially, and sublimes completely with slight blackening and evolution of isobutylamine. If heated rapidly to a temperature somewhat higher than its melting point, it melts easily without sensible decomposition.

Diisobutyl platinochloride, $2N(C_4H_9)_2H,H_2PtCl_6$, is obtained in long, dark-red channelled prisms by mixing a concentrated solution of platinic chloride with a saturated solution of diisobutylamine hydrochloride and allowing the liquid to stand.

Triisobutylamine platinochloride, $2N(C_4H_9)_3,H_2PtCl_6$. The hydrochloride is first prepared by the action of concentrated hydrochloric acid on the amine, but combination takes place very slowly. The liquid is then evaporated to a syrup, taken up with a little ethyl alcohol, and mixed with concentrated platinic chloride solution. A precipitate of small orange prisms forms immediately, and if the liquid is filtered after 24 hours it gradually deposits large, ruby-coloured crystals with very brilliant facets.

The differences in crystalline form between the platinochloride of diisobutylamine and triisobutylamine are so well marked that the two compounds can readily be separated mechanically after they have been crystallised together from a mixture. C. H. B.

Isobutaldehyde and its Polymeric Modification. By G. A. Barbaglia (*Gazzetta*, **16**, 430—437).—Isobutaldehyde is readily polymerised by adding to it a small quantity of iodine, the mixture being

kept cool. The rapidity of the conversion is dependent on the quantity of iodine, the lowering of the temperature, and the purity of the aldehyde; a slight variation in the conditions makes a considerable difference in the time required for the change. Even under the most favourable conditions, however, the conversion is never complete. It is difficult to explain the peculiar function of the iodine, and the author classifies the phenomenon among the so-called "catalytic changes." As regards its nature, the trimolecular or polymeric modification of the isobutaldehyde differs from the simpler or monomolecular form, in that the latter is characterised by its susceptibility to chemical change as evidenced by its oxidisability, its combination with ammonia and the alkaline hydrogen sulphites, and its conversion into the isothiobutaldehyde and isobutyric acid, whereas the former is unaltered by oxidising agents, as also by ammonia and the alkaline bisulphites, and is not readily altered by sulphur.

The polymeric modification crystallises in glistening prisms melting at 59·5° with partial sublimation, it boils at 195·2° (at 752 mm.) with but slight alteration. If heated for some time in a sealed tube at 150°, it is partially reconverted into isobutaldehyde.

Isobutaldehyde, even of a high degree of purity, becomes polymerised spontaneously after a time. V. H. V.

Action of Sulphur on Aldehydes. By G. A. Barbaglia (*Gazzetta*, **16**, 426—430).—In the course of the preparation of thiovaleraldehyde from sulphur and valeraldehyde (Abstr., 1881, 34), the author observed the formation of a substance which crystallises in slender prisms, melts at 94·5°, and is insoluble in water, very soluble in alcohol and ether. More recent analytical results indicate that this compound is a trithiovaleraldehyde, $C_5H_6S_3$; this might be formed as follows: $C_5H_{10}S + 2S_2 = C_5H_6S_3 + 2H_2S$; the compound having the structural formula—

$$CH_2\cdot CH\cdot CH\cdot CH\cdot CHS.$$
$$\quad\quad\quad

a compound also obtained by the direct action of bromine on ethylene mercaptan. It forms insoluble crystals, decomposing at 151—154° with carbonisation. Its isomeride, *diethylidene tetrasulphide*,

$$CHMe<\begin{matrix}S\cdot S\\S\cdot S\end{matrix}>CHMe,$$

is prepared by the oxidation of thialdine hydrochloride by iodine dissolved in potassium iodide. It forms an amorphous flocculent precipitate. V. H. V.

Action of Nitrous Acid on Ketones. By L. Claisen (*Ber.*, **20**, 252).—Nitrosoketones have hitherto only been obtained by indirect methods; the author now finds that they can be obtained directly by the action of free or nascent nitrous acid on the ketones. For instance, nitrosoacetone is obtained in considerable quantity by adding hydrochloric acid to a mixture of amyl nitrite and acetone, and heating on the water-bath. In like manner, when a well-cooled mixture of acetophenone and amyl nitrite is saturated with hydrogen chloride, a white crystalline mass separates which melts at 133—134°, and seems to be nitrosoacetophenone hydrochloride. Amyl nitrite reacts also with aldehydes, yielding products now under investigation. A. J. G.

Derivative of Dimethylene Disulphone. By W. Autenrieth (*Ber.*, **20**, 373—376).—Duplosulphacetone, $S_2(:CMe_2)_2$ (Wislicenus, *Zeit. für Chem.*, 1869, 224), is prepared as follows:—50 grams of acetone (from bisulphite compound) are heated at 120—130° with 50 grams of phosphorus trisulphide for 6—8 hours, the product poured into water and steam-distilled. The oil is dried over calcium chloride and redistilled; it boils between 180° and 190°. It yields an additive compound with methyl iodide.

Tetramethyldimethylene disulphone, $CMe_2<\begin{matrix}SO_2\\SO_2\end{matrix}>CMe_2$, is obtained by oxidising duplosulphacetone by means of potassium permanganate. It is extracted by ether. It crystallises from hot alcohol in slender, white needles melting at 220—225° with decomposition. It dissolves readily in alcohol, ether, and chloroform, sparingly in hot water. Concentrated sulphuric and nitric acids dissolve it unchanged. It is not changed when boiled with aqueous alkali; prolonged heating with concentrated alkali decomposes it completely. N. H. M.

γ-Amidovaleric Acid. By J. Tafel (*Ber.*, **20**, 249—251).—In a previous communication (Abstr., 1886, 1008) it was suggested that the substance C_3H_9NO, obtained by heating γ-amidovaleric acid, was a *oxymethylpyrrolidine* having the formula $<\begin{matrix}CHMe\cdot NH\\CH_2—CH_2\end{matrix}>CO$ or $<\begin{matrix}CHMe\cdot N\\CH_2\cdot CH_2\end{matrix}>C\cdot OH$; this hypothesis is now confirmed, as it is shown to yield a methylpyrrolidine on reduction; there is, however, as yet no evidence as to which of the two formulæ is correct.

Methylpyrrolidine, $<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>NH$, is obtained by adding sodium

to a boiling solution of oxymethylpyrrolidine in amyl alcohol as long as hydrogen is evolved. It is a colourless, mobile liquid, boils at 96—97° under a pressure of 737 mm. (mercurial column in vapour), but volatilises rapidly at the ordinary temperature, and has a penetrating, stupefying odour; the vapour quickly produces violent headache.

The use of Ladenburg's reduction method for the removal of oxygen seems to be generally applicable not only to the pyrroline but also to the pyridine and quinoline series, seeing that by it non-oxygenated bases have been prepared from oxylepidine, methylepidone, and carbostyril (Knorr and Klotz, this vol., p. 278).

A. J. G.

Hydroxybutyric Acid in Diabetic Urine. By E. Stadelmann (*Zeit. Biol.*, **32**, 456—459).—The preparation of the salts of hydroxybutyric acid in a pure state from the urine of diabetic patients is a matter of some difficulty, as they become mixed with a dark-coloured sticky mass, which is probably composed of derivatives of diabetic sugar, and which is soluble in ether. It becomes black on evaporation.

According to Minskowski the preparation of the silver salt is that which presents least difficulties. The author finds that the zinc salt is prepared with greater ease. The sugar is best removed by means of fermentation (see Külz, this vol., p. 290), but this method is not without its drawbacks, as putrefactive decomposition is apt to occur simultaneously.

Putrefaction was prevented by adding salicylic acid to the extent of 0·2 per cent., and also by letting the fermentation take place in a cool cellar. At the end of a fortnight the urine showed no signs of putrefaction and all the sugar had disappeared from 55 litres, the quantity used. Another difficulty arises from the quantity of urea, which in these cases is very abundant in the urine. The method adopted for getting rid of it was as follows:—1½ kilos. lime was added to the total quantity of urine, much ammonia came off, and after five hours the filtered liquid still showed a diminished but still a high percentage of urea; it was, therefore, evaporated down to 20 litres, when more ammonia was evolved, another kilo. of lime was added, and heat applied for 30 hours, at the end of which time no more ammonia was given off; the remaining quantity of urea was removed by mercuric nitrate. From the clear, greenish-yellow filtrate, the zinc salt of hydroxybutyric acid was then prepared and crystallised; the brown colour beforementioned was, however, still present; the crystals were therefore treated with absolute alcohol, in which they are but sparingly soluble, while the coloured mass dissolves easily. An advantage of this calcium hydroxide process is that by its means the sulphates and phosphates are also removed. The salicylic acid used in the process is removed by washing the zinc salt with alcohol.

W. D. H.

β-Bromolevulinic Acid. By I. Wolff (*Ber.*, **20**, 425—433).—In order to determine the constitution of the isomeric angelolactones produced by the distillation of levulinic acid, the reactions were studied of the bromolevulinic acid obtained both from α-angelo-

lactone bromide and directly from levulinic acid. When treated with sodium carbonate, this bromo-acid yields acetoacrylic acid, so that its constitution is expressible by the formula $COMe{\cdot}CHBr{\cdot}CH_2{\cdot}COOH$, and the angelolactone from which it is derived by $<^{-CH_2{\cdot}CO-}_{CH\,:\,CMe}>O$. Acetoacrylic acid, $CHAc\,:\,CH{\cdot}COOH$, forms glistening scales, melting at 125—125·5°, sparingly soluble in alcohol and chloroform; it combines with phenylhydrazine and also with bromine to form α-β-dibromolevulinic acid; this crystallises in needles melting at 107—108°, and is readily soluble in alcohol, ether, and benzene. Simultaneously with acetoacrylic acid a hydroxylevulinic acid is formed, an oily liquid, which, when heated with ammonia, yields a base, $C_8H_{12}N_2$, besides two subsidiary products not as yet investigated. This base, which is also obtained from bromolevulinic acid, is identical with the dimethyl ketone of Gutnecht and Treadwell; it crystallises from water as a hydrate, $C_8H_{12}N_2,3H_2O$, in white lustrous needles, melting with loss of water at 74—77°, and when dried over desiccating substances is converted into brittle, lustrous prisms of the anhydrous base; this melts at 86° and boils at 190°; the hydrochloride, $C_8H_{12}N_2,HCl + 2H_2O$, melts at 91°; the platinochloride crystallises in glistening needles. The *methiodide*, $C_8H_{12}N_2,MeI + 2H_2O$, is a citron-yellow, crystalline substance. It seems that the dimethyl ketone contains four methyl-groups and may be represented by a formula $C_4Me_4N_2$; in confirmation, the silver salt of a tetracarboxylic acid, $C_4(COOH)_4N_2$, has been obtained.

Bromolevulinic acid, when heated with aniline, yield a base, $C_{20}H_{22}N_2$, which crystallises in silky needles melting at 107—108°, soluble in alcohol, ether, and chloroform.

In conclusion, it is remarked that the above-mentioned dimethyl ketone, or azo-ketone, the benzoimide of Erdmann, the base, $C_{28}H_{20}N_2$, obtained by Japp and Wilson (Trans., 1886, 825), and isoindole, can be represented as derived from a fundamental substance, $C_4H_4N_2$, which it is proposed to call pyrazine. The above substances will then be its tetra- and di-methyl-, tetra- and di-phenyl-derivatives respectively. V. H. V.

Composition and Constitution of Arabinosecarboxylic Acid and Arabinose. By H. Kiliani (*Ber.*, **20**, 282 and 339—346; compare this vol., p. 229).—When the lactone of arabinosecarboxylic acid is boiled with concentrated hydriodic acid (15 parts) and amorphous phosphorus, a product is obtained consisting chiefly of normal caprolactone and a small quantity of normal caproic acid. Arabinosecarboxylic acid is therefore *pentahydroxycaproic acid*, $C_6H_{12}O_7$, and not hexahydroxyheptylic acid, and has the same composition as gluconic and galactonic acids. When the lactone of arabinosecarboxylic acid is digested with nitric acid (sp. gr. 1·2) for 24 hours at 50°, the product diluted and evaporated, a viscous substance is obtained which when dissolved in a little warm water solidifies on cooling to a hard cake of crystals. This is redissolved, the oxalic acid present precipitated with lime, and the filtrate evaporated; it separates in long, colourless needles. This compound is a *double*

lactone of *metasaccharic acid*, and has the formula $C_6H_6O_6 + 2H_2O$. It differs from saccharic acid in having a neutral reaction. It is soluble in 8 parts of cold water, insoluble in ether, sparingly in alcohol. The *calcium salt*, $C_6H_8O_8Ca + H_2O$, forms microscopic spheres. When the solution of the hydrogen potassium salt is exposed to air, it acquires an intense red colour. When the double lactone is reduced by means of hydriodic acid, a small quantity of an acid is formed which melts at about 200°; this when treated with sodium amalgam is converted into an acid, probably adipic acid. The lactone has probably the constitution

$$<^{-\,CO\cdot O\,-}_{CH(OH)}>CH\cdot CH<^{-\,CO\cdot O\,-}_{CH(OH)}>.$$

The above experiments show that arabinose has the formula $C_5H_{10}O_5$, and not $C_6H_{12}O_6$ and the fact that it yields with hydrocyanic acid a compound containing a normal carbon-chain, shows further that it is an aldehyde of normal pentahydroxypentane:

$$OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO.$$

The formation of arabonic acid from arabinose is readily explained, being analogous to that of gluconic acid.

Small quantities of arabinosecarboxylic acid are best prepared by saturating the solution from which the amide has separated with dry hydrogen chloride, and, after 12 hours, evaporating with baryta-water; the barium is then precipitated by sulphuric acid, the hydrochloric acid by silver oxide, and the solution evaporated to a syrup. During treatment with hydrochloric acid, the solution should be cooled with ice. The yield is 70 to 80 per cent. N. H. M.

Action of Nitric Acid on Bibasic Acids. By H. P. N. Franchimont (*Rec. Trav. Chim.*, **5**, 281—289).—In continuation of experiments on the action of nitric acid on substituted malonic acids (Abstr., 1886, 533), the author has more fully examined this reaction in the case of methylmalonic acid. The products obtained were carbonic anhydride, acetic acid, and *trinitroethane*, the last of which forms brilliant crystals, melting at 55°, sparingly soluble in water, volatile in the air, and volatilising rapidly in steam. Attempts were made to prepare trinitro- from bromo-dinitroethane, but without success. The trinitro-compound is also formed in small quantities in the reaction between nitric and isosuccinic acids. In the case of amylmalonic acid, no appreciable quantity of a nitro-derivative of a hydrocarbon was obtained, but only carbonic anhydride and hexylic acid. Thus the action of nitric acid on substituted malonic acids consists mainly in the production of a monobasic acid containing two atoms of carbon less than the original substance, and the evolution of 2 mols. of carbonic anhydride for each molecule of the substance employed.

V. H. V.

Isonitroso-compounds. By H. Bergreen (*Ber.*, **20**, 531—534).—The author finds that ethyl isosuccinate, when treated with nitrous acid, yields ethyl isonitrosopropionate (Abstr., 1878, 659). Ethylic ethylmalonate and ethyl benzylmalonate, when similarly

treated, yield oily compounds, from which pure crystalline substances have not yet been obtained. W. P. W.

Action of Phosphoric Chloride on Ethyl Acetonedicarboxylate. By B. S. Burton and H. v. Pechmann (*Ber.*, **20**, 145—149).—*β-Chloroglutaconic acid*, $COOH\cdot CH : CCl\cdot CH_2\cdot COOH$, is obtained by gradually adding 50 grams of ethyl acetonedicarboxylate to 160 grams of phosphorus pentachloride, and then heating the whole on a water-bath. The product is poured into water, the oil extracted with ether, and the ethyl salt so obtained saponified by boiling for two or three hours with 20 to 25 times the amount of strong hydrochloric acid. The acid melts at 129° and becomes dark at 170°, is readily soluble in water, ether, and alcohol, less soluble in chloroform, from which it separates in groups of white needles; it is also soluble in boiling benzene. When reduced by zinc-dust and acetic acid, an acid melting at 132° (the m. p. of glutaconic acid) is formed; it decomposes at a higher temperature with evolution of gas. Chloroglutaconic acid is reduced by sodium amalgam to glutaric acid.

Glutic acid, $COOH\cdot C : C\cdot CH_2\cdot COOH$, is formed when 5 grams (1 mol.) of the chlorinated acid dissolved in alcohol is gradually dropped into and shaken with a 5 per cent. alcoholic solution of potash containing rather more than the theoretical amount (3 mols.) of potash. The potash solution is previously heated at 50—60°. It is filtered, washed with alcohol, and dried. The united products of several preparations are treated with a large excess of dilute sulphuric acid and extracted with ether. The acid is purified by washing with warm benzene and crystallising from a mixture of ether and benzene. It forms groups of slender needles which melt at 145 — 146° with evolution of carbonic anhydride; it is readily soluble in water, alcohol, and ether, insoluble in chloroform and benzene. It decomposes when kept long. When a solution of the hydrogen potassium salt is heated, carbonic anhydride is evolved, and there is an odour of acetone. The *lead salt* forms a white precipitate; the *barium* and *potassium salts* crystallise in slender needles and in long, flat needles respectively; both contain water of crystallisation. N. H. M.

Aconitic Acid. By W. Hentschel (*J. pr. Chem.*, **35**, 205—206).—Aconitic acid is readily obtained when crystallised citric acid (2 parts) is heated with sulphuric acid (2 parts) and water (1 part) for 4—6 hours in a reflux apparatus; the yield amounts to 35—45 per cent. of the citric acid employed. Acetone is also formed in the reaction, and gas is evolved consisting of 2 vols. carbonic anhydride and 1 vol. carbonic oxide. W. P. W.

Reduction of Dihydroxytartaric Acid Diphenylhydrazine. By J. Tafel (*Ber.*, **20**, 244—249).—*Phenylhydrazineamidooxalacetic acid*, $COOH\cdot CH(NH_2)\cdot C(:N_2HPh)\cdot COOH$, is obtained by the reduction of an alkaline solution of dihydroxytartaric acid diphenylhydrazide by the addition of successive small quantities of sodium amalgam until the intense yellow solution is just decolorised; it could not be

obtained in a state approaching purity, but when heated with sulphuric acid it is converted into the corresponding *anhydride*, $C_{10}H_9N_3O_3$. This crystallises in snow-white plates of fatty lustre, is insoluble in ether and hot water, sparingly soluble in hot alcohol, benzene, acetic acid, and acetone, more readily in chloroform and hot concentrated hydrochloric acid; it dissolves readily in alkalis and alkaline carbonates, and in concentrated sulphuric acid. The solutions become red or violet on exposure to air. The alkaline solution reduces Fehling's solution on gently heating, and mercuric oxide in the cold, the solution in the latter case showing an intense orange-red coloration. From its reactions, it is very probably *amido-oxyquinizinecarboxylic acid*.

If the reduction of the diphenylhydrazide with sodium amalgam is pushed further, Lehrfeld's diamidosuccinic acid (Abstr., 1882, 162) is obtained. A. J. G.

Gluconic Acid. By L. Boutroux (*Compt. rend.*, **104**, 369—370).—The crystallised ammonium gluconate recently described by Volpert (*Ber.*, **19**, 2621) had previously been obtained by the author, and described by him as ammonium zymogluconate. Zymogluconic acid obtained from glucose by acid fermentation (Abstr., 1883, 682), is, however, identical with the gluconic acid of Hlasiwetz and Habermann. C. H. B.

Constitution of Trimethylenetricarboxylic Acid. By A. Michael (*J. pr. Chem.* [2], **35**, 132—136).—When ethyl sodiomalonate is treated with ethyl α-bromacrylate by Conrad and Limpach's method, a very violent reaction takes place, and an ethyl salt is formed identical with that obtained by Conrad and Guthzeit from ethyl α-β-dibromopropionate. The latter compound must therefore have the constitution $CH_2 : C(COOEt)\cdot CH(COOEt)_2$.

When treated with sodium ethoxide and benzoic chloride, no substitution took place; the ethyl salt was recovered unchanged. This behaviour is analogous to that of the compound obtained by Perkin from ethylene bromide and ethyl sodiomalonate. This negative result can therefore no longer hold good as evidence against the constitution $CH_2\cdot CH\cdot CH(COOEt)_2$ for ethyl vinaconate. N. H. M.

Amides of Ethylsulphonic Acid. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, **5**, 274—280).—In continuation of the experiments of Romburgh on the action of nitric acid on the replaced amides of phenylsulphonic acid, corresponding derivatives of ethylsulphonic acid are described, and the action on them of nitric acid is investigated. As regards the preparation of ethylsulphonic acid, preference is given to the oxidation of ethyl bisulphide. The acid is converted into the chloride, which is dissolved in ether, and an ethereal solution of the amine added. The amide formed is then fractionally distilled. The mono- and di-methylamides of ethylsulphonic acid, and the corresponding ethyl-compounds, are all colourless liquids, miscible with water, and of peculiar odour. Their physical properties are given in the following table:—

	Boiling point.	Specific gravity.
Ethylsulphonomethylamide, $EtSO_2{\cdot}NHMe$	276°	1·216
Ethylsulphonodimethylamide, $EtSO_2NMe_2$	240	1·146
Ethylsulphonethylamide, $EtSO_2NHEt$ ..	272	1·154
Ethylsulphonodiethylamide, $EtSO_2NEt_2$ ..	254	1·080

Ethylsulphonomethylamide, when treated with nitric acid (sp. gr. 1·5), yields a nitramide, $EtSO_2{\cdot}NMe{\cdot}NO_2$, a colourless liquid solidifying at 11°; it cannot be distilled without decomposition, and deflagrates with violence when heated at 100°. Ethylsulphonodimethylamide yields under the same conditions nitrodimethylamine. So also ethylsulphonethylamide yields a nitramide, $EtSO_2{\cdot}NEt{\cdot}NO_2$, a crystalline substance melting at 15°, sparingly soluble in water. The same compound is also obtained from ethylsulphonodiethylamide.

Thus the action of nitric acid on the replaced amides of ethylsulphonic acid is precisely analogous to the action on the corresponding derivatives of phenylsulphonic acid. V. H. V.

Calcium Urate. By S. Delépin (*Physiol. Soc.*, 1887, 2—3).—Urine containing calcium oxalate, with perhaps an excess of uric acid, sometimes contains small acicular crystals differing from the generally known urates. They sometimes occur also in the urine of gouty subjects. Crystals of uric acid and natural sediments of acid urates when allowed to stand in hard water become transformed into small masses of acicular crystals very insoluble even in hot water. This change does not occur when distilled water is used. This led to the conclusion that the crystals were urate of calcium, and that this salt might be of more importance in the economy than has been supposed. Pure urate of calcium was therefore prepared from uric acid and calcium hydroxide, and a crystalline substance was obtained similar in appearance to the crystals observed in urine, and formed by adding hard water or calcium hydroxide to a deposit of uric acid or urates in urine.

Urate of calcium is colourless or white when seen in large quantities. It forms long, needle-shaped crystals which are generally grouped in stars, but it may also be amorphous. It is more insoluble in hot water than other urates, and less easily decomposed by acids. Strong acid, however, like sulphuric acid, displaces the uric acid, which crystallises readily. The murexide reaction is easily obtained.

It was also found that in gouty deposits in the cartilages, which are generally spoken of as sodium urate, urate of calcium was found to be present in all cases, both by chemical tests and microscopical appearances. W. D. H.

Chloropyromucic Acid. By H. B. Hill and L. L. Jackson (*Ber.*, **20**, 252—255).—When ethyl pyromucate tetrachloride, prepared in the cold, is treated with concentrated alcoholic soda, sodium β-γ-dichloropyromucate is in the main formed; if, however, in the preparation of the tetrachloride, the temperature has been allowed to rise too high, further substitution occurs, and the sodium salts obtained

contain not inconsiderable quantities of sodium trichloropyromucate. *β-γ-Dichloropyromucic acid*, $C_5H_2Cl_2O_3$, crystallises in slender interlaced needles, melts at 168—169°, is readily soluble in alcohol, ether, and hot water, moderately in boiling benzene or chloroform. The following salts are described:—Barium ($+ 3H_2O$), calcium ($+ 4H_2O$), silver and potassium (both anhydrous). The *ethyl* salt crystallises in slender needles and melts at 176°; the *amide* also crystallises in slender needles and melts at 176°. The free acid when treated with bromine-vapour does not give a stable additive compound, but is converted with evolution of bromine into an acid of high melting point (dichlorobromopyromucic acid ?). With bromine-water, it is converted into mucochloric acid with evolution of carbonic anhydride. It is only completely oxidised with nitric acid after boiling for several hours; monochloric and dichloromaleic acids were identified amongst the products of the reaction. A. J. G.

Transformation of Furfuran into Pyrroline. By F. Canzoneri and V. Oliveri (*Gazzetta*, **16**, 486—497).—Although it is generally assumed that furfuran, C_4H_4O, and pyrroline are derivatives of a fundamental group, C_4H_4, yet the transformation of one into the other has not as yet been effected. When pyromucic acid is heated with ammoniacal zinc chloride and lime, and the products of the change are collected successively in a tube surrounded by a freezing mixture, in another containing hydrochloric acid, and a third containing bromine, there are obtained pyrroline, furfuran, and methylamine hydrochloride. The last is a product of a more profound change. The formation of pyrroline results in the displacement of oxygen by the NH-grouping, thus: $C_4H_4O + NH_3 = C_4H_5N + OH_2$. Its identity was established by the analysis of its potassium-derivative and by the pyrroline-red reaction. The furfuran was obtained as a colourless mobile liquid, of ethereal odour, boiling at 32°.

In order to throw some further light on the relative arrangement of the atoms in the C_4H_4 residue, the authors have effected the synthesis of α-naphthylamine by heating in sealed tubes pyromucic acid, lime, zinc chloride, and aniline; this result tends to show that the atoms are arranged thus: CH:CH·CH:CH. Further, as furfuran undergoes condensation with the benzene nucleus with elimination of water, it may probably be regarded as a glycide or rather as an anhydride of the unsaturated glycol CH(OH):CH·CH:CH·(OH). V. H. V.

Furfurylamine. By J. Tafel (*Ber.*, **20**, 398—400).—This compound is easily obtained by the reduction of C. Fischer's phenylfurfurazide (Abstr., 1878, 310) with sodium amalgam and acetic acid, as follows:—45 grams of phenylfurfurazide is dissolved in 600 grams of alcohol and then 1350 grams of $2\frac{1}{2}$ per cent. sodium amalgam slowly added, the solution being kept constantly acid by the addition of acetic acid, and the temperature not being allowed to rise above 3°. The product is then supersaturated with potash, and, after driving off the alcohol, is steam-distilled. The distillate is acidified with hydrochloric acid and evaporated to a small bulk. A red resin separates, and the filtrate, after being made slightly alkaline, is treated with

ether to remove aniline, re-acidified, and evaporated until crystallisation commences. The residue is then mixed with dry powdered potash and distilled. Furfurylamine distils over as a colourless liquid, boiling at 135° under 754 mm. The *hydrochloride* is easily soluble in water, alcohol, and hydrochloric acid; but this latter solution does not turn green when heated as stated by Ciamician and Dennstedt. The *sulphate* forms minute needles, the *acid oxalate*, $C_5H_7NO,C_2H_2O_4 + \frac{1}{2}H_2O$, characteristic narrow scales. The *picrate* forms golden-yellow prisms which decompose without previous fusion at 150°. When exposed to the air, the amine absorbs carbonic anhydride, forming a crystalline mass melting at 75° and decomposing at a higher temperature with evolution of carbonic anhydride. L. T. T.

Thiophen in Aniline. By M. T. Leko (*Chem. Centr.*, 1887, 41).—The author endeavoured to find an amido-compound of thiophen in aniline by converting commercial aniline into the phenylhydrazine compound, and testing this for thiophen. The results were negative. G. H. M.

Reduction of α-Thiophenic Acid. By F. Ernst (*Ber.*, **20**, 518—520).—α-Thiophenic acid is the sole product of the oxidation of propiothiënone, and is best prepared by this method; when reduced with sodium amalgam in alkaline solution, it yields *tetrahydro-α-thiophencarboxylic acid*, $C_4SH_7{\cdot}COOH$. This acid crystallises in large, tabular, colourless laminæ, melts at 51° (corr.), has an intensely acid taste, and an intolerable odour; it is very readily soluble in water and alcohol, and is volatile with steam. It is decomposed on distillation, shows all the properties of a hydro-acid, and, like the tetrahydrodicarboxylic acid (this vol., p. 237), gives the indophenine reaction on heating. The *methyl* salt is a colourless, oily liquid, boiling at 206° without decomposition; the *ethyl* salt is a yellow liquid. The *calcium* salt, $(C_4SH_7{\cdot}COO)_2Ca + 3H_2O$, is crystalline; the *silver* salt, $C_4SH_7{\cdot}COOAg$, forms small, glistening crystals, sparingly soluble in water. W. P. W.

Constituents of Coal-tar. By K. E. Schulze (*Ber.*, **20**, 409—414).—The author finds that amongst the benzene-derivatives (hydrocarbons and phenols) present in coal-tar, meta-compounds largely predominate. Thus, for instance, of the trimethylbenzenes the 1 : 3 : 5 compound (containing 3 meta-positions) is very largely in excess of the 1 : 3 : 4 and 1 : 2 : 3 compounds (containing each 1 meta-position: and the quantity of metacresol is much larger than that of ortho- or para-cresol.

The author has isolated from coal-tar pyridine, Ladenburg's α-α-lutidine (Abstr., 1885, 557), α-γ-lutidine, and γ-picoline. L. T. T.

Reciprocal Transformation of Cumene- and Cymene-derivatives. By M. Fileti (*Gazzetta*, **16**, 497—503).—This paper is merely an answer to Widman's criticisms (this vol., p. 133) on the author's view regarding the mutual transformations of cumene- and cymene-derivatives. V. H. V.

Oxidation of the Methyl Ethers of Mono- and Di-bromo-orthoisopropylphenols. By A. Peratoner (*Gazzetta*, **16**, 420—424).—Methyl bromisopropyl oxide, when heated with nitric acid of sp. gr. =1·3, yields dibromo- and nitrobromo-methoxysalicylic acids, $OMe{\cdot}C_6H_2Br_2{\cdot}COOH$, and $OMe{\cdot}C_6H_2Br(NO_2){\cdot}COOH$; it appears that the greater part of the compound is completely burnt in the oxidation process, and the formation of a dibromo- from a monobromo-compound is due to the subsequent action of bromine liberated by the nitric acid.

Methyldibromisopropylphenyl oxide, under similar treatment, yields dibromomethoxysalicylic acid, identical with that obtained above. V. H. V.

Compound of Orthotoluidine with Cupric Chloride. By E. Pomey (*Compt. rend.*, **104**, 365—366).—Orthotoluidine is mixed with hydrochloric acid, and, after combination has taken place, a saturated solution of cupric chloride in hydrochloric acid is added to the warm liquid, an abundant, pale-yellow, crystalline precipitate is formed. This is recrystallised from hydrochloric acid and dried below 100°, at which temperature it begins to decompose. It has the composition $CuCl_2,5(C_7H_9N,HCl)$, and is very soluble in water. The copper is completely precipitated from the solution by potassium hydroxide, and the chlorine by silver nitrate.

The compound which paratoluidine hydrochloride forms with cupric chloride contains 2 mols. of the former to 1 mol. of the latter. C. H. B.

Compound of Paratoluidine with Cupric Chloride. By E. Pomey (*Compt. rend.*, **104**, 300).—If cupric chloride is added to a solution of paratoluidine it produces a brown precipitate, but if both solutions contain free hydrochloric acid no precipitate is formed. If, however, the mixture is heated to boiling and is then allowed to cool, it deposits very brilliant, golden-yellow crystals which are purified by recrystallisation from hydrochloric acid, and are then dried at 100° until no more hydrogen chloride is given off. They have the composition $CuCl_2,2(C_7H_9N,HCl)$, and are soluble in water. C. H. B.

Thioparatoluidine. By J. Truhlàr (*Ber.*, **20**, 664—679, and *Chem. Centr.*, 1887, 8—10).—*Thioparatoluidine* melts at 103—104°, and is basic. When an alcoholic solution is treated with an excess of hydrobromic acid, the hydrobromide, $C_{14}H_{16}N_2S,2HBr$, is thrown down. It forms small, white needles, easily soluble in hot alcohol, less soluble in cold alcohol, and easily in water. The hydriodide is obtained in a corresponding manner; it forms light-brown needles easily soluble in water, alcohol and ether; when heated at 100°, it is decomposed with separation of iodine.

Thioparacetotoluide, $NHAc{\cdot}C_6H_3Me{\cdot}S{\cdot}C_6H_3Me{\cdot}NHAc$, is obtained by treating thioparatoluidine with an excess of acetic anhydride; it crystallises from alcohol in snow-white, stellate groups of needles, and melts at 211°; it is easily soluble in alcohol and benzene, less easily in ether, and insoluble in water.

Thioparabenzoyltoluide, $NHBz{\cdot}C_6H_3Me{\cdot}S{\cdot}C_6H_3Me{\cdot}NHBz$, is obtained

by warming thioparatoluidine with excess of benzoic chloride as long as hydrochloric acid is evolved. It crystallises from alcohol in snow-white, brilliant needles, easily soluble in alcohol, benzene, and ether, and melts at 186°.

Hydroxythiotoluene, $S(C_6H_3Me{\cdot}OH)_2$, is obtained by boiling diazothioparatoluidine hydrochloride with water, saturating the solution with sodium chloride, dissolving the precipitated substance in alkali, and again precipitating with dilute sulphuric acid. It can also be obtained by dissolving the crude product in benzene and fractionally precipitating with light petroleum. It forms a brown powder, soluble in alcohol, ether, and benzene; it melts at 135°.

Thioparatolylthiocarbamide, $S<\begin{matrix}C_6H_3Me{\cdot}NH\\C_6H_3Me{\cdot}NH\end{matrix}>CS$, is obtained by treating an alcoholic solution of thioparatoluidine with excess of carbon bisulphide. Hydrogen sulphide is evolved and, after some time, colourless crystals mixed with crystals of sulphur separate. The latter are removed by means of carbon bisulphide. The substance is insoluble in all ordinary solvents, but dissolves in strong nitric and sulphuric acids. It melts at 234—235°. Another very stable substance is formed at the same time; it melts at 231°. Attempts to prepare thioparatolylsulphocarbanil from it were unsuccessful.

The *picrate* of thioparatoluidine, $C_{14}H_{16}N_2S,2C_6H_2(NO_2)_3OH$, is obtained in aggregates of fine needles by evaporating alcoholic solutions of thioparatoluidine and picric acid. It crystallises from benzene in stellate needles with brilliant lustre, and melts at 179°. When quickly heated, it explodes.

Dithioparatolyldicarbamide, $S<\begin{matrix}C_7H_6{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_7H_6\\C_7H_6{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_7H_6\end{matrix}>S$, is obtained as a yellow, amorphous powder, together with thioparatoluidine hydrochloride, by passing carbonyl chloride (1 mol.) into a solution of thioparatoluidine (2 mols.) in benzene. By solution in alcohol and reprecipitation, it forms a whitish, amorphous powder which is decomposed at 130°. It is only slightly soluble in ether and in cold alcohol, but easily in hot. It is not acted on by concentrated hydrochloric acid, but is soluble in strong nitric and sulphuric acids.

G. H. M.

Secondary and Tertiary Quinones. By R. Nietzki and F. Kehrmann (*Ber.*, **20**, 322—328).—When sodium rhodizonate (Abstr., 1885, 1127) is dissolved in dilute hydrochloric acid and treated with an orthotoluylenediamine salt, the *compound* $\begin{matrix}CO{\cdot}C(OH):C{\cdot}N\\|\quad\quad\quad|\ |\\CO{\cdot}C(OH):C{\cdot}N\end{matrix}>C_7H_6$ is obtained. It is a gelatinous substance, sparingly soluble in water, readily in alcohol. Alkali solutions dissolve it with a fine violet colour. When oxidised with dilute nitric acid, it is converted into a derivative of triquinoyl, *diquinoyltolazine*,

$$\begin{matrix}CO{\cdot}CO:C{\cdot}N\\|\quad\quad\quad|\ |\\CO{\cdot}CO:C{\cdot}N\end{matrix}>C_7H_6 + 2H_2O.$$

This forms yellow needles, almost insoluble in cold water, ether, and

alcohol, readily soluble in warm glacial acetic acid. When the compound $C_{13}H_6N_2O_4$ is warmed with an excess of an orthotoluylenediamine salt, *benzotritolazine*, $C_6(N_2 : C_7H_6)_3$, is obtained. This is a yellow, crystalline substance, very readily soluble in alcohol and in chloroform; it crystallises from the latter in long needles (with 1 mol. $CHCl_3$). It has feeble basic properties.

When sodium rhodizonate, dissolved in water, is treated with an excess of a salt of orthotoluylenediamine and sodium acetate, a compound is obtained containing three toluylenediamine-groups; when oxidised, it is converted into the triazine, $C_{27}H_{18}N_6$, already described.

The above experiments show that triquinoyl contains six quinone oxygen-atoms. It is probable that the hydroxyl-groups in rhodizonic acid have the para-position. This view being accepted, the fact that adjacent oxygen-atoms react like an orthoquinone-group and are independent of para-oxygen, forms an important support for the ketonic formulæ of quinones. N. H. M.

Preparation of Dimethylaniline on a Large Scale. By P. Schoop (*Chem. Zeit.*, **11**, 253—254).—The author describes the preparation of dimethylaniline from aniline, wood spirit, and hydrochloric acid. It is important to use pure materials, therefore the aniline is tested by quantitative fractional distillation, by its sp. gr., and by its solubility in hydrochloric acid; the wood spirit must be free from acetone and ethyl alcohol, and is tested by the iodoform test. The materials are mixed in the proportions of 93 parts of aniline, of which 18 are saturated with hydrochloric acid, and 75 parts of methyl alcohol. The excess of methyl alcohol and the comparatively small quantity of hydrochloric acid tend to produce a purer oil. With more hydrochloric acid, the reaction takes place at a lower temperature, but there is danger of the formation of toluidine. The mixture is heated in a closed vessel, the temperature (from 270—230°) and pressure (of which a table is given in the paper) being carefully regulated; a fall of pressure with a constant temperature (230°) indicates the completion of the operation. The product consists of an oily and watery portion which are separated; the latter is then treated with soda and the oil which separates is removed, the alkaline water being finally distilled and the oil from this collected in a separate receiver. Each of these three lots of oil is rectified by itself, the product obtained from the first lot being the best and that from the third the worst. Many modes of testing the purity of the product are given; it is especially important to have a pure substance for the preparation of green dyes. D. A. L.

Ortho- and Para-chlorodimethylaniline. By T. Heidlberg (*Ber.*, **20**, 149—151).—*Orthochlorodimethylaniline*, $C_6H_4Cl{\cdot}NMe_2$, is obtained by Staedel's method, which consists in heating the hydrobromide of the chloraniline with rather more than 2 mols. of methyl alcohol at 145°. It is a clear, colourless liquid boiling at 206—207°. The *hydrochloride* forms white, hygroscopic needles; the *platinochloride* crystallises in lustrous yellow prisms. *Nitrosorthochlorodimethylaniline* crystallises from alcohol in yellow needles.

Parachlorodimethylaniline was prepared by Sandmeyer's method:

50 grams of amidomethylaniline was dissolved in 82 grams of hydrochloric acid; 300 c.c. of water is added and then a solution of 26 grams of sodium nitrite in 60 c.c. of water. The whole is added to a boiling solution of 10 per cent. cuprous chloride solution. It crystallises in large, lustrous, flat needles, soluble in alcohol, ether, and benzene, insoluble in water; it melts at 230—231°. The *hydrochloride* is a syrup which crystallises with difficulty; the ferrocyanide forms microscopic prisms. The *platinochloride*, $(C_6H_4Cl\cdot NMe_2)_2,H_2PtCl_6$, crystallises in gold-coloured prisms. *Nitrosoparachlorodimethylaniline* crystallises in splendid, orange-yellow needles melting at 56°; it is soluble in alcohol, ether, and benzene, &c. Like the ortho-compound it is a very feeble base. N. H. M.

Carvole-derivatives. By H. Goldschmidt and E. Kisser (*Ber.*, **20**, 486—492).—Carvylamine (this vol., p. 249), a primary amine, is a colourless liquid, and yields a benzoyl-derivative which crystallises in white needles melting at 169°. The *hydrochloride*, $C_{10}H_{17}N,HCl$, crystallises from absolute alcohol in small, white, silky needles, and melts at about 180° with decomposition; when heated with sodium nitrite, an oil, probably identical with Leuckart's carveol, is obtained (this vol., p. 376).

From carvole, by the action of dry hydrogen chloride, hydrochlorocarvole, $C_{10}H_{15}OCl$, is obtained; this decomposes on distillation with evolution of hydrogen chloride, and when treated with hydroxylamine yields hydrochlorocarvoxime (Abstr., 1885, 1058). The phenylhydrazine-derivative, $C_{10}H_{15}Cl : N_2HPh$, crystallises in small, white prisms, and melts at 137°. When a mixture of carvole and ethyl acetoacetate in equimolecular proportions is treated with hydrogen chloride, the product poured into water and afterwards extracted with ether, two compounds are obtained, one an oil, and the other a crystalline substance of the formula $C_{16}H_{25}ClO_4$, which forms lustrous, white, hard prisms, melts at 146°, and does not yield a derivative with acetic chloride.

The constitution of carvole is now represented by the formula $CPr\lessgtr^{CH\cdot CO}_{CH:CH}>CHMe$, and that of limonene by the formula

$$CPr\lessgtr^{CH\cdot CH_2}_{CH:CH}>CHMe.$$

W. P. W.

Action of Aromatic Diamines on Sugars. By P. Griess and G. Harrow (*Ber.*, **20**, 281—282).—The diamidobenzenes and their carboxylic acids react with some sugars to form compounds analogous to those obtained by Fischer with phenylhydrazine and sugars. Those with the orthodiamine are especially interesting, as they are relatively easily prepared and show well-characterised physical properties.

If, for instance, concentrated aqueous solutions of orthophenylenediamine (1 part) and dextrose (2 parts) are mixed, a few drops of hydrochloric acid added, and the whole allowed to remain eight days in a moderately warm place, a feebly basic substance is formed. This crystallises in lustrous, white needles, which are moderately soluble in

hot water and alcohol; it also dissolves very readily in hydrochloric acid, and is reprecipitated unaltered from the solution by ammonia. It has a bitter taste, and reduces Fehling's solution. If in the above reaction the corresponding γ-diamidobenzoic acid [COOH : $(NH_2)_2$ = 1 : 2 : 3] is substituted for the diamine, a substance having the character of an amido-acid is obtained. It crystallises in lustrous, white plates, is very sparingly soluble even in boiling water or alcohol, does not reduce Fehling's solution to any marked extent, and behaves like sugars when heated in a tube. A very similar acid was prepared from maltose. A. J. G.

Action of Orthotoluylenediamine on Dextrose. By O. Hinsberg (*Ber.*, **20**, 495—497).—An almost quantitative yield of a condensation-compound, $C_{19}H_{30}N_2O_{10}$, is obtained when an alcoholic solution of orthotoluylenediamine (1 mol.) is heated with dextrose (2 mols.) on a water-bath. The compound crystallises from dilute alcohol in slender, white, silky needles, which become brown when heated at 100° in a capillary tube, and melt at about 160° with evolution of gas; it is readily soluble in water, sparingly soluble in alcohol and ether, and gives a red coloration with ferric chloride. A loss of about 4 per cent. in weight occurs if the compound is heated at 100°, and it then gives figures showing a slightly lower percentage of carbon. Dilute alkalis are without action on it, but mineral acids, on warming if dilute, reconvert it into orthotoluylenediamine and, probably, dextrose. The constitution of this compound is probably

$$C_7H_6(N : C_6H_{12}O_5)_2,$$

and its instability in the presence of acids raises the question whether the view that dextrose contains the aldehyde-group is correct. Other aromatic diamines yield compounds analogous to dextrose; no well-crystallised compound can be obtained from orthotoluylenediamine and lactose. W. P. W.

Tetramidobenzene and its Derivatives. By R. Nietzki and E. Hagenbach (*Ber.*, **20**, 328—338).—*Diethenyltetramidobenzene*, $C_6H_2(<^{-N}_{NH}>C_2H_3)_2$, is obtained by reducing diacetyldinitroparaphenylenediamine with hydrochloric acid and tin. It crystallises in long, colourless needles, sparingly soluble in cold water, readily in hot water and in alcohol. It melts at 210°. The *platinochloride*, $C_{10}H_{10}N_4,H_2PtCl_6 + H_2O$, crystallises in long gold-coloured needles; the *sulphate* (with 1 mol. H_2O) crystallises from hot water in colourless needles almost insoluble in alcohol. When the sulphate is dissolved in fuming nitric acid (5 parts), a *mononitro-derivative*, $C_{10}H_9N_4{\cdot}NO_2 + \frac{1}{2}H_2O$, is obtained; this forms orange-red needles melting at 276°. The *platinochloride*, $C_{10}H_9N_5O_2,H_2PtCl_6 + \frac{1}{2}H_2O$, crystallises in long, gold-coloured needles.

Ethenylnitrotriamidobenzene, $C_2H_3<^{NH}_{N--}>C_6H_2(NH_2){\cdot}NO_2$, is formed when diacetyldinitrophenylenediamine is heated with alcoholic ammonia

at 150°. It melts at 295—300°. The *hydrochloride* and *sulphate* were prepared.

Ethenyltetramidobenzene, $C_2H_3\leqslant^{NH}_{N-}>C_6H_2(NH_2)_2$, is obtained by reducing the nitrotriamido-compound with stannous chloride and hydrochloric acid. It only exists in the form of its salts. The picrate crystallises in sparingly soluble yellow needles.

Diacetyldinitrometaphenylenediamine, $C_6H_2(NHAc)_2(NO_2)_2$, is obtained by treating diacetylmetaphenylenediamine with nitric acid (sp. gr. 1·533); it forms pale-yellow needles which melt at 228°. *Dinitrometaphenylenediamine* is prepared by heating the acetyl-derivative with dilute sulphuric acid. It is an orange-yellow substance, sparingly soluble in alcohol; it melts at about 300°.

Tetramidobenzene, $C_6H_2(NH_2)_4$ [= 1 : 2 : 4 : 5], is formed when freshly prepared dinitrometaphenylenediamine is added to a warm, strongly acid solution of stannous chloride containing an excess of metallic tin. The *hydrochloride* is very soluble in water, sparingly in hydrochloric acid. The *dinitrate*, $C_6H_2(NH_2)_4,2HNO_3$, forms small, green needles. All the salts absorb oxygen from the air, becoming blue-violet or brown. When the nitrate or hydrochloride is treated with sodium carbonate solution, the *base* is obtained in small, brown needles.

The constitution ascribed to tetramidobenzene is shown by the fact that the diethenyltetramidobenzene from metaphenylenediamine is not identical with that obtained from paraphenylenediamine, and that the nitrogen of the diethenyltetramidobenzene from paraphenylenediamine must be attached to adjacent carbon-atoms.

Diethenyltetramidobenzene, obtained by reducing dinitrodiacetylmetaphenylenediamine, melts above the range of the thermometer. The *sulphate* and *platinochloride* were prepared.

Tetramidobenzene reacts with phenanthraquinone, with formation of the *compound* $C_{14}H_8\langle^{N}_{N}\rangle C_6H_2(NH_2)_2$. This is a feeble base, and dissolves in sulphuric acid with a greenish-blue colour which changes to violet and red when diluted. N. H. M.

Carbonylorthamidophenol and Thiocarborthamidophenol. By S. v. Chetmicki (*Ber.*, **20**, 177—179).—When ethyl thiocarbamidophenol, C_7H_5NOS, is heated with strong hydrochloric acid at 156—160°, amidophenol, mercaptan, and carbonic anhydride are formed; the formation of mercaptan can only be explained on the supposition that the ethyl-group in the thiocarbamidophenol is combined with sulphur. Thiocarbamidophenol dissolved in hydrochloric acid, when oxidised with chloride of lime, yields a bisulphide, $S_2(C_6H_4\langle^{N}_{O}\rangle C)_2$; the same compound is also formed when the sodium salt of thiocarbamidophenol is treated with iodine solution. These results confirm the formula $C_6H_4\langle^{N}_{O}\rangle C\cdot SH$, ascribed by Kalckhoff to thiocarborthamidophenol.

The reactions of carbonylorthamidophenol point to the constitution $C_6H_4<^{NH}_{-O-}>CO$.

N. H. M.

Displacement of the Amido-group in Aromatic Compounds by Hydrothionyl and Oxysulphuryl. By P. Klason (*Ber.*, **20**, 349—350).—When diazosulphonic acids are treated in small quantities with warm alcoholic solution of potassium sulphide, nitrogen is evolved, and the diazo-group is displaced by SH; in this way thiocresolsulphonic acid was prepared. The sulphonic acids can be readily purified by precipitating with an ammoniacal solution of lead acetate, and decomposing the lead salt by means of hydrogen sulphide.

When the thiophenolsulphonic acids are treated with potassium permanganate in the cold, toluenedisulphonic acids are formed in which oxysulphuryl has taken the place occupied by the amido-group in the original amido-acid.

The method above described can be employed for introducing selenium and probably also tellurium into aromatic compounds.

N. H. M.

Halogen-derivatives of Azobenzene and Hydrazobenzene. By J. V. Janovsky and L. Erb (*Ber.*, **20**, 357—362; compare Abstr., 1886, 1024).—*Parabromazobenzene* is the chief product obtained by brominating azobenzene dissolved in glacial acetic acid. It melts at 82°, and can be sublimed; it dissolves readily in alcohol, ether, and acetone, less in light petroleum. When the alcoholic solution is treated with ammonia and then with hydrogen sulphide, a *hydrazobromo-compound* is formed which crystallises in lustrous plates, melting at about 115°.

Dinitromonobromazobenzene, $C_{12}H_7(NO_2)_2BrN_2$, and *nitroparabromazobenzene*, $C_{12}H_8(NO_2)BrN_2$, are obtained by nitrating parabromazobenzene; the former crystallises in orange-red, sparingly soluble needles; the latter forms yellow needles readily soluble in alcohol. When parabromazobenzene is dissolved in fuming sulphuric acid at 140°, a *sulphonic acid* is formed identical with the parabromoparasulphonic acid of azobenzene previously described (*Sitzungsber. Akad. Wissen.*, 1884, 647).

Metabromazobenzene is prepared from the product obtained by the action of bromine on azobenzene by extracting the precipitated bromides with a little 80 per cent. alcohol. It forms yellowish-green, lustrous plates, readily soluble in alcohol, ether, and acetone; it melts at 53—56°. *Metabromazobenzeneparasulphonic acid* is obtained by heating a solution of metabromazobenzene in fuming sulphuric acid (5 parts) at 160°. It crystallises in plates with a golden lustre. The *potassium salt* crystallises in yellow, lustrous, microscopic needles. The *sodium salt* is sparingly soluble.

Nitrazobenzene, $NPh:N\cdot C_6H_4\cdot NO_2$, is obtained by dissolving azobenzene (20 grams) in 100 c.c. of glacial acetic acid, heating at 100°, and adding 25 c.c. of nitric acid (sp. gr. 1·51). The product is filtered and purified by crystallising from a mixture of acetone and alcohol. It forms orange-yellow, microscopic needles, readily soluble in alcohol,

&c. It melts at 122—123°. When the alcoholic solution is boiled with alkali, it acquires a splendid emerald colour. The *sulphonic acid* forms hygroscopic needles; the solution of the acid gives with potassium carbonate a purple-red precipitate consisting of woolly needles; with sodium salts a green, and with silver salts a red precipitate.

Nitrazoxybenzene is prepared by nitrating azobenzene at 75°. It crystallises from alcohol, ether, chloroform, and acetone in red plates, melting at 127°.

Hexazoxybenzene, $C_{24}H_{18}N_6O$, is formed when orthonitrazobenzene or nitrazoxybenzene (m. p. 127°) is reduced with sodium amalgam. It is almost insoluble in ether, alcohol, and acetone, readily in boiling benzene, toluene, and xylene, separating therefrom in orange-coloured plates. Warm fuming sulphuric acid dissolves it with a violet-blue colour. N. H. M.

Direct Substitution Products of Parazotoluene; Hydrazobromobenzenes, and Hydrazobromotoluenes. By J. V. Janovsky and L. Erb (*Ber.*, **20**, 362—364).—When 10 grams of parazotoluene dissolved in 200 c.c. of glacial acetic acid is gradually treated with 15 c.c. of nitric acid (sp. gr. 1·5), and the product precipitated with water and dissolved in hot alcohol, two nitro-compounds are obtained. The one crystallises in orange-yellow, monoclinic needles melting at 114°, the other separates from the mother-liquor as an oil which gradually crystallises. When parazotoluene is treated directly with fuming nitric acid in the cold, two nitro-products are also formed, one of which is sparingly soluble in alcohol and acetone, and forms honey-coloured monoclinic crystals melting at 185—187°. It is a dinitrazotoluene, and is possibly identical with that described by Petrieff (*Jahresber.*, 1873), to which, however, the melting point 110° is ascribed. No mononitro-compound melting at 76° (Petrieff, *loc. cit.*) could be obtained.

By the action of bromine on a boiling solution of azotoluene, a bromide crystallising in large, ruby-coloured prisms, melting at 138·5°, is formed; it is probably identical with Petrieff's monobromide (m. p. 136°). The mother-liquor from the bromide yielded a second bromide melting at 115°.

Parabromhydrazobenzene, $NHPh{\cdot}NH{\cdot}C_6H_4Br$, is prepared by reducing parabromazobenzene with alcoholic solution of hydrogen ammonium sulphide. It crystallises from dilute alcohol in lustrous scales which melt at 115°. It is very stable in the air, and only becomes slightly coloured in four to six weeks. When treated with sulphuric acid, and the sulphate thus obtained decomposed with ammonia, a *monobromobenzidine* is obtained which crystallises in silvery plates.

Dibromohydrazobenzene melting at 82° was obtained from diorthobromazobenzene.

Bromoparahydrazotoluene was prepared in a similar manner from bromoparazotoluene; it melts at 117°. N. H. M.

Action of Acetone on Paramidoazobenzene. By C. Engler and C. Schestopal (*Ber.*, **20**, 480—482).—When acetone (1 mol.) is

heated with paramidoazobenzene hydrochloride (2 mols.) in sealed tubes at 150—160° for two to three days, methane is formed together with a solid condensation product from which hydrochloric acid extracts a base, $C_{17}H_{15}N_3$; this is probably a quinoline or benzidine derivative, and after fractional precipitation with aqueous potash and distillation in a vacuum is found in the fraction boiling at 280°. It crystallises in bright yellow needles, melts at 204—205°, and is soluble in alcohol and ether; the aqueous solutions of its salts show a strong blue fluorescence. The *sulphate*, $C_{17}H_{15}N_3,H_2SO_4$, crystallises from aqueous alcohol in small, monoclinic prisms, and is very soluble in water; the *chromate*, $C_{17}H_{15}N_3,H_2Cr_2O_7$, forms orange-yellow, crystalline aggregates; and the *platinochloride*, $C_{17}H_{15}N_3,H_2PtCl_6$, crystallises in golden-yellow, flat needles sparingly soluble in cold water.

When reduced with tin and hydrochloric acid, a well-crystallised stannochloride of a base is obtained; this base crystallises in brilliant white needles, melts at 185°, dissolves readily in alcohol and ether, and yields well-crystallised salts. W. P. W.

Action of Phenol on Diazoamidobenzene. By K. Heumann and L. Oeconomides (*Ber.*, **20**, 372—373).—When diazoamidobenzene is heated on a water-bath with phenol, parahydroxyazobenzene is formed together with aniline. Resorcinol, and α- and β-naphthol react in a similar manner. N. H. M.

Constitution of Safranines. By A. Bernthsen (*Ber.*, **20**, 179—180).—The constitution previously suggested (this vol., p. 139) for the safranines is supported by the explanation of the constitution of toluylene-red (p. 139). The author considers the unsymmetrical formula proposed by Witt and by Nietzki (this vol., p. 250) as the most probable. N. H. M.

Manufacture of Methylene-blue. By O. Mühlhäuser (*Dingl. polyt. J.*, **262**, 371—379).—For the production of methylene-blue on a large scale two processes are in use: (1.) Oxidation of dimethyl-paraphenylenediamine in acid solution, in presence of hydrogen sulphide (Caro's method); (2.) Oxidation of a base containing sulphur, obtained by the action of hydrogen sulphide on nitroso-dimethylaniline dissolved in strong sulphuric acid (Oehler's process). The author describes in detail the manufacture of methylene-blue by the "soda waste" and "zinc sulphide" processes. The former comprises the following operations:—(1.) Preparation of a solution of nitrosodimethylaniline by treating dimethylaniline with hydrochloric acid, and nitrating the hydrochloride thus obtained. (2.) Treatment of the nitrosodimethylaniline with soda waste in order to reduce the nitroso-compound to an amine. (3.) Oxidation with ferric chloride. (4.) Extraction of the raw colour with salt and zinc chloride solution. (5.) Filtration.

The zinc sulphide process.—When hydrogen sulphide is passed into sulphuric acid of 40—50° B., sulphur is deposited and sulphurous anhydride evolved thus: $H_2SO_4 + H_2S = SO_2 + S + 2H_2O$. On bringing the sulphurous anhydride into contact with hydrogen

sulphide further precipitation of sulphur takes place according to the following equation: $SO_2 + 2H_2S = 2H_2O + 3S$. When these reactions occur in the presence of nitrosodimethylaniline sulphate a colourless base containing sulphur is obtained, yielding a blue dye on oxidation. The methylene-blue obtained in this manner is said to be purer and stronger in tinctorial power than that yielded by the soda waste process. D. B.

Thiophen-green. By L. E. Levi (*Ber.*, **20**, 513—517).—*Tetramethyldiamidodiphenylthiënylmethane*, $C_4SH_3{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, the leuco-base of thiophen-green, is obtained by heating a mixture of thiophenaldehyde (1 part) and dimethylaniline (2 parts) with a small quantity of alcohol at 100° for six hours, and gradually adding three to four parts of zinc chloride. The base crystallises in compact needles, melts at 92—93°, and is insoluble in water, readily soluble in ether, benzene, toluene, and alcohol; the alcoholic solution very quickly becomes coloured green on exposure to the air. The *platinochloride* has the formula $C_{21}H_{24}N_2S,H_2PtCl_6$; the *picrate*,

$$C_{21}H_{24}N_2S,2C_6H_2(NO_2)_3OH,$$

forms yellowish-green needles, melts at about 208°, and is sparingly soluble in cold water, readily soluble in alcohol, ether, &c.; the *methiodide*, $C_{21}H_{24}N_2S,2MeI$, crystallises from alcohol and water in white scales, and melts at 210—212°.

When the leuco-base is oxidised, preferably with manganese dioxide and dilute sulphuric acid, *thiophen-green*, $C_4SH_3{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}OH$, is obtained as a dark-brown, uncrystallisable oil, insoluble in water, but soluble in alcohol, benzene, chloroform, and, when recently prepared, in ether; it cannot be distilled. Thiophen-green forms salts with the elimination of the elements of 1 mol. of water. The *zinc* salt, $3(C_{21}H_{22}N_2S),ZnCl_2 + 2H_2O$, crystallises in scales showing a beautiful coppery lustre, and is readily soluble in all ordinary solvents; the solution in water is coloured a deep bluish-green, which becomes reddish-yellow on adding an acid. The colour imparted to silk and wool very nearly resembles that produced by benzaldehyde-green, but is somewhat more yellow. The *picrate*,

$$C_{21}H_{22}N_2S,2C_6H_2(NO_2)_3{\cdot}OH,$$

forms scales showing a coppery lustre, and is very sparingly soluble in water; the *sulphate*, $C_{21}H_{22}N_2S,H_2SO_4$, crystallises in beautiful scales, readily soluble in water; and the *oxalate*,

$$2(C_{21}H_{22}N_2S),3H_2C_2O_4 + 2H_2O,$$

crystallises in scales showing a metallic lustre, is readily soluble in water, alcohol, &c., and decomposes very readily. W. P. W.

Action of Phosphorus Pentachloride on Acetanilide. By A. Michael (*J. pr. Chem.* **35**, 207—208).—When phosphorus pentachloride is allowed to act on acetanilide at moderate temperatures, compounds very different in composition to the unstable chloroderivatives described by Gerhardt and by Wallach are obtained.

Thus, when a mixture of acetanilide (1 mol.) and phosphorus pentachloride (3 mols.), after the first reaction is over, is allowed to remain at the ordinary temperature until evolution of hydrogen chloride has practically ceased, then heated at 100° to complete the reaction, and poured into water, a compound, $C_8H_8Cl_2N_2$, is formed, which crystallises in large, white, monoclinic prisms, melts at 116·5—117°, is insoluble in water, soluble in alcohol, and shows both acid and basic properties. If, instead of completing the reaction at 100°, the mixture is allowed to remain in the cold for some time longer, and then poured into water, long, citron-yellow needles of a compound $C_{38}H_{36}Cl_7N_4$ are obtained. This melts at 227—229°, is soluble in alcohol, and shows both acid and basic properties. Two other compounds are also formed in this reaction, one of which crystallises in large tables, whilst the other is a thick liquid which only becomes solid after long standing.

The author finds that acetamide, when treated with 2 mols. of phosphorus pentachloride and subsequently with water, yields a compound in the form of a thick liquid. W. P. W.

Action of Hydroxylamine and Phenylhydrazine on Dialdehydes and Ketones. By F. Münchmeyer (*Ber.*, **20**, 507—513).—Isophthalaldehyde reacts with hydroxylamine hydrochloride and soda to form the *aldoxime* $C_6H_4(CH : NOH)_2 = [1 : 3]$; this crystallises in lustrous, white scales, melts at 211—212°, and is soluble in alcohol and ether. When treated with an excess of acetic chloride, isophthalaldoxime yields metadicyanobenzene; the *methyl*-derivative, $C_6H_4(CH : NOMe)_2$, crystallises in colourless needles melting at 77°, the *ethyl*-derivative in small needles melting at 165°.

Orthophthalaldehyde (which, according to a foot-note by V. Meyer, has been recently obtained by Faust, and will shortly be described), when heated with hydroxylamine hydrochloride and soda, yields *orthophthalaldoxime*, $C_6H_4(CH : NOH)_2$ [1 : 2], it crystallises in small needles, melts at 245°, and is soluble in alcohol.

Tetramethyldiamidobenzophenone, although it reacts with hydroxylamine hydrochloride (Abstr., 1886, 877), does not yield a hydrazide when treated either with phenylhydrazine or its hydrochloride; further investigation of the action of these reagents on amidophenones shows that this behaviour is exceptional. When β-dinitrobenzophenone is heated with hydroxylamine hydrochloride and soda, the *oxime* is obtained in small, golden-yellow needles melting at 205—207°; and by treatment with phenylhydrazine hydrochloride the ketone yields a *hydrazide*, $(C_6H_4NO_2)_2C : N{\cdot}NHPh$, this is a red powder melting at 219—220°, and is soluble in acetic acid, sparingly soluble in hot alcohol. β-Diamidobenzophenone under these conditions yields a crystalline *oxime* melting at 177—178°, and a *hydrazide*, $(NH_2{\cdot}C_6H_4)_2C : N_2HPh$, in the form of yellow needles melting at 183°. Also, when similarly treated, paramidoacetophenone is converted into an *oxime* crystallising in small needles which melt at 147—148°; and the hydrochloride of a *hydrazide*, $NH_2{\cdot}C_6H_4{\cdot}CMe : N_2HPh,HCl$, which is crystalline, and evolves gas when heated at 205—207°. W. P. W.

Preparation of Vanillin from Metachloroparanitrobenzaldehyde. By L. Landsberg (*Dingl. polyt. J.*, **262**. 139).—It is proposed to convert metachloroparanitrotoluene into chloronitrobenzyl chloride or bromide, and to treat the latter with lead or copper nitrate, in order to obtain metachloroparanitrobenzaldehyde. On treating this aldehyde with an alkaline methoxide or the hydroxide dissolved in methyl alcohol, the chlorine is displaced by the methoxyl-group with formation of metamethoxyparanitrobenzaldehyde. The same compound is obtained when the chlorine in metachloroparanitrobenzaldehyde is displaced by hydroxyl, and the resultant hydroxynitrobenzaldehyde converted into its methyl ether. Metamethoxyparanitrobenzaldehyde crystallises from boiling water in white needles melting at 62°, and is converted into vanillin according to the known methods. When heated with acetic anhydride or sodium acetate, it is resolved into metamethoxyparanitrocinnanic acid, melting at 218°. D. B.

Action of Potassium Ferricyanide on Acetophenone. By K. Buchka and P. H. Irish (*Ber.*, **20**, 386—395).—All attempts to obtain phenylglyoxylic acid by the oxidation of acetophenone have hitherto proved unavailing, the methyl-group always being eliminated and benzoic acid produced. The author finds that by the continued action of an alkaline solution of potassium ferricyanide on acetophenone, phenylglyoxylic acid is produced. The quantity is, however, very small, and appears to be due to a secondary reaction, and not to direct oxidation, a great deal of benzoic acid being formed.

When 3 grams of acetophenone are added to a solution of 50 grams of potassium ferricyanide and 5 grams of potassium hydroxide in half a litre of water, and the whole allowed to stand for about 12 hours, small quantities of a crystalline substance are deposited. This substance, when recrystallised from benzene, is obtained in minute colourless needles having the formula $C_{16}H_{15}O_2N$. When heated with caustic potash, ammonia is evolved, and the *potassium* salt $C_{16}H_5O_4K$ of a new acid is produced; it crystallises in minute needles. The corresponding *barium salt* yields concentric groups of needles, and contains $3\frac{1}{2}$ mols. H_2O. The free *acid* is crystalline, and melts at 99—101° (uncorr.). The compound $C_{16}H_{15}O_2N$ thus seems to be the nitrile of the acid. Both the acid and the nitrile dissolve in concentrated sulphuric acid with a violet-red coloration, but the coloration is destroyed by dilution. The coloration produced by dissolving phenylglyoxylic acid in strong sulphuric acid is, on the other hand, not destroyed by dilution. By continued boiling with concentrated potash, both the nitrile and the acid yield phenylglyoxylic acid and acetophenone.

The author is inclined to think that the formation of these compounds is due to a part of the acetophenone becoming oxidised to benzaldehyde, which then unites with undecomposed acetophenone and hydrocyanic acid to form a cyanhydrin; Ph·COH + Ph·COMe + HCN = CPhMe(OH)·CPh(OH)·CN.

Other mixed aromatic and fatty ketones seem to act in a similar way towards alkaline ferricyanide. These reactions are being further studied. L. T. T.

Metacyanobenzoic Acid. By W. Brömme (*Ber.*, **20**, 524—530).—The *silver*, *barium* (with $3\frac{1}{2}$ mols. H_2O), *calcium* (with 3 mols. H_2O), and *zinc* salts are described; the *methyl* salt melts at 65°, and is sparingly soluble in alcohol, ether, benzene, and carbon bisulphide, sparingly soluble in water; the *ethyl* salt melts at 56° (comp. Müller, Abstr., 1886, 802); and the *amide* melts above 300°, and is soluble in alcohol and ether, insoluble in water. Metacyanobenzoic acid does not yield a nitro-derivative when treated with nitric acid or with a mixture of nitric and fuming sulphuric acids, and is neither reduced by sodium amalgam nor by sodium under various conditions. An alcoholic solution of hydroxylamine hydrochloride and soda converts the acid into the *amidoxime* (*loc. cit.*).

When metacyanobenzoic acid is dissolved in strong aqueous ammonia and the solution saturated with carbon bisulphide, a crystalline acid, $(COOH\cdot C_6H_4\cdot C : NH)_2S$, is obtained, which melts at 199°, and is soluble in hot water, alcohol, and ether. When reduced with zinc and hydrochloric acid, this compound is converted into an acid of the formula $(COOH\cdot C_6H_4\cdot CH_2)_2NH$ [1 : 3]; it is crystalline, melts above 300°, sublimes without decomposition, and is sparingly soluble in hot water, soluble in alcohol, ether, benzene, and carbon bisulphide. The *zinc* salt is very hygroscopic, and is readily soluble in all ordinary solvents. An acid of the formula

$$(COOH\cdot C_6H_4\cdot C : NH)_2O,$$

is formed when metacyanobenzoic acid and benzene are added to fuming sulphuric acid, allowed to remain for 24 hours, and then poured into cold water; it is crystalline, melts above 300°, shows both acid and feeble basic properties, and is soluble in alcohol and ether, insoluble in water. The *silver* salt, $C_{16}H_8O_5N_2Ag_4$, is insoluble in water. W. P. W.

Behaviour of Cyanobenzoic Acids on Dry Distillation. By W. Brömme (*Ber.*, **20**, 521—524).—Why dry calcium metacyanobenzoate is submitted to dry distillation, metadicyanobenzene is obtained in addition to benzonitrile; the melting point of the dicyanobenzene is 157·5°. If, however, calcium paracyanobenzoate is similarly treated, benzonitrile and paradicyanobenzophenone are obtained.

Paradicyanobenzophenone, $CO(C_6H_4\cdot CN)_2$ [CN : CO = 1 : 4], crystallises in nodules, melts at 204·5, sublimes without decomposition, and is sparingly soluble in hot water and light petroleum, soluble in carbon bisulphide, readily soluble in alcohol, ether, and benzene. With phenylhydrazine, it yields a *triphenylhydrazide*; this crystallises in nodules, melts at 212°, is soluble in alcohol, ether, &c., and when heated is decomposed into the ketone.

Benzophenoneparadicarboxylic acid, $CO(C_6H_4\cdot COOH)_2$, formed by hydrolysis of the ketone, sublimes without previous fusion, is very sparingly soluble in ether and benzene, sparingly soluble in alcohol, soluble in hot water to the extent of 1 in 50,000, and is obtained from this solution in microscopic needles. The *methyl* salt crystallises in large needles, and melts at 138°; the *silver* salt, $C_{15}H_8O_5Ag_2$ +

Ag_2O, prepared by hydrolysis of the pure methyl salt, is insoluble in water. The acid and its methyl salt show a remarkable similarity to terephthalic acid and methyl terephthalate respectively.

Benzonitrile forms a solid compound when treated with phenylhydrazine. W. P. W.

Meta- and Para-hydroxynitrobenzoic Acids. By P. Griess (*Ber.*, **20**, 403—409).—Of the four possible meta-hydroxynitrobenzoic acids [COOH : OH : NO_2 = 1 : 3 : 6, 1 : 3 : 4, 1 : 3 : 2, and 1 : 3 : 5], the author has already described the first three under the names of α-, β-, and γ-metahydroxynitrobenzoic acids respectively; and also one of the two possible parahydroxynitrobenzoic acids, 1 : 4 : 3 and 1 : 4 : 2 (the former), under the name δ-hydroxynitrobenzoic acid (*Ber.*, **5**, 856, and Abstr., 1879, 246). Gerland (*Annalen*, **91**, 192) has described the formation of a hydroxynitrobenzoic acid by the dissolution of metahydroxybenzoic acid in nitric acid of sp. gr. 1·36. The author finds that in this way di- or tri-nitro-compounds are always produced, but by employing only a slight excess of very dilute acid, a mixture of mononitro-compounds may be obtained; this contains three isomerides, his α- and β-acids, and a third ζ-hydroxynitrobenzoic acid, which is undoubtedly the missing acid, 1 : 3 : 5. The separation of the three acids is effected by means of the sparing solubility of the β-acid in water, and the greater solubility of the barium salt of the γ-acid than of that of the ζ-acid.

ζ-Hydroxynitrobenzoic acid,

$$C_6H_3(NO_2)(OH)_2{\cdot}COOH\ [COOH : OH : NO_2 = 1 : 3 : 5],$$

crystallises in white scales or plates. It is easily soluble in alcohol, ether, and boiling water, melts at 167°, and decomposes at a higher temperature with evolution of black fumes. It has an acid and astringent taste; its barium salt crystallises with $6H_2O$ in pale-yellow prisms. The acid to which Grube and Hübner ascribe the above formula (*Ber.*, **10**, 1704) is, the author considers, undoubtedly identical with V. Meyer and Michler's diazoxybenzoic acid (*Ber.*, **3**, 746).

Barth's parahydroxynitrobenzoic acid, obtained by dissolving parahydroxybenzoic acid in nitric acid of sp. gr. 1·46 (*Zeit. f. Chem.*, 1866, 647), is identical with the author's δ-acid. L. T. T.

Derivatives of Orthamidophenylvaleric Acid. By L. Diehl and A. Einhorn (*Ber.*, **20**, 377—386).—*Orthamidocinnamenylpropionic acid*, $NH_2{\cdot}C_6H_4{\cdot}CH : CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is prepared by dissolving orthamidocinnamenylacrylic acid in 50 parts of water in presence of alkali, and adding 5 per cent. sodium amalgam gradually; the solution must be kept almost neutral by addition of sulphuric acid. In 3 or 4 days it is treated with sulphuric acid, filtered, saturated with ammonia, and evaporated to dryness on a water-bath; ammonia is given off, and the free acid is extracted from the residue by absolute alcohol. The alcoholic solution is treated with water, heated to drive off the alcohol, and cooled with ice; the acid separates with 1 mol. H_2O. The ethereal solution shows green fluorescence.

Orthamidodibromophenyl-γ-δ-dibromovaleric acid,

$$NH_2{\cdot}C_6H_2Br_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained by adding a solution of bromine in glacial acetic acid to a cooled solution of orthamidocinnamenylpropionic acid, also in glacial acetic acid. The product is poured into water containing sulphurous acid, and the precipitated substance dried and recrystallised from chloroform. It forms microscopic needles, which melt at 167°, with decomposition. It is readily soluble in alcohol, ether, and glacial acetic acid, less soluble in chloroform, insoluble in carbon bisulphide, water, and dilute mineral acids. Aqueous alkali solutions dissolve it readily.

Orthamidodibromophenylvaleric acid, $NH_2{\cdot}C_6H_2Br_2{\cdot}(CH_2)_4{\cdot}COOH$, is formed when a solution of orthamidotetrabromophenylvaleric acid in 5 parts of alcohol and 2 parts of strong hydrochloric acid, is treated with granulated zinc for a quarter of an hour, and then poured into water. It is extracted with ether, and the oil thus obtained dissolved in the smallest possible amount of 10 per cent. aqueous caustic soda and warmed. The acid crystallises from aqueous alcohol in splendid long needles (with 1 mol. H_2O). It melts at 96°, and decomposes with evolution of gas at 223°. It dissolves readily in the usual solvents, except cold water, in which it is insoluble. The alkali salts are readily soluble. *Ethyl orthamidodibromophenylvalerate hydrochloride*, $C_{13}H_{18}NO_2Br_2Cl$, forms slender, white needles, which melt at 135—136°. The *acetyl-derivative*, $C_{13}H_{15}NO_3Br_2$, crystallises from 80 per cent. hot alcohol in tufts of slender, white needles, melting at 205—206°. It is readily soluble. The *ethyl salt* of the acetyl compound crystallises from dilute alcohol in stellate groups of needles. It melts at 139°, dissolves readily in alcohol, ether, &c., more sparingly in benzene, and can be distilled in small quantities without decomposition.

Orthamidophenylvaleric acid, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is obtained by reducing orthamidodibromophenylvaleric acid dissolved in absolute alcohol with sodium amalgam. The product is made slightly acid with hydrochloric acid, treated with water, and boiled until free from alcohol. It is then made slightly ammoniacal, evaporated repeatedly until no more ammonia comes off, and the free acid thus obtained is crystallised from water containing a little alcohol. It forms white needles, melting at 60—62°. N. H. M.

Substituted Mono- and Di-bromosalicylic Acids. By A. Peratoner (*Gazzetta*, **16**, 405—420).—In this paper are described a series of substituted mono- and di-bromosalicylic acids, obtained by heating the methyl salts of the mono- and di-bromo-acids with the alkyl iodides in presence of potash.

Methyl bromosalicylate, $OH{\cdot}C_6H_3Br{\cdot}COOMe$ [COOMe : OH : Br = 1 : 2 : 5], obtained by the bromination of methyl salicylate dissolved in carbon bisulphide, crystallises in colourless needles or small prisms of the trimetric system, melting at 61°, and boiling without decomposition at 264—266°, insoluble in water, sparingly soluble in methyl alcohol. On hydrolysis, it yields a bromosalicylic acid melting at 164—165°.

Methyl methoxybromosalicylate, $OMe \cdot C_6H_3Br \cdot COOMe$, obtained by the methylation of the above, crystallises in colourless needles melting at 39—40°, and distilling without decomposition at 295°, insoluble in water, soluble in other menstrua. The corresponding *acid* crystallises in long needles melting at 119°, resembling the methyl salt, as regards its solubility. Its alkaline salts are very soluble, the *calcium*, *magnesium*, and *silver* salts crystallise in needles.

Ethoxybromosalicylic acid, $OEt \cdot C_6H_3Br \cdot COOH$, crystallises in colourless needles melting at 130°; its metallic salts resemble those of the methoxy-acid; the methyl salt crystallises in colourless needles, melting at 49°, and boiling at 300—302°.

Propoxybromosalicylic acid, $OPr^{\alpha} \cdot C_6H_3Br \cdot COOH$, melts at 62°; its *methyl* salt is a colourless liquid boiling at 321—324°, and solidifying in a freezing mixture; the isopropyl acid, $OPr^{\beta} \cdot C_6H_3Br \cdot COOH$, crystallises in needles melting at 101°.

Methoxydibromosalicylic acid,

$$OMe \cdot C_6H_2Br_2 \cdot COOH \ [COOH : OMe : Br : Br = 1 : 2 : 3 : 5],$$

crystallises in long needles melting at 193—194°, and its barium salt, with $2 \cdot 5H_2O$, in grouped needles; the methyl salt forms colourless needles melting at 53°. Methyl dibromosalicylate,

$$OH \cdot C_6H_2Br_2 \cdot COOMe,$$

obtained as one of the products of the bromination of methyl salicylate, crystallises in long needles, melting at 148—149°.

Ethoxydibromosalicylic acid, $OEt \cdot C_6H_2Br_2 \cdot COOH$, crystallises in colourless needles melting at 155—156°, and its methyl salt in interlaced needles melting at 43°.

None of the above described acids give any coloration with ferric chloride. V. H. V.

Constitution of Dibromosalicylic Acid. By A. Peratoner (*Gazzetta*, **16**, 401—404).—The dibromosalicylic acid, obtained by the direct bromination of salicylic acid, when heated in sealed tubes with dilute sulphuric acid (1 : 3), yields the dibromophenol melting at 36° (40° Körner), the constitution of which is known to be [OH : Br : Br = 2 : 3 : 5]; the carboxylic acid must then be represented by the formula [COOH : OH : Br : Br = 1 : 2 : 3 : 5]. Tribromo- and 1 : 2 bromophenol are also formed as subsidiary products in the above reaction: their formation is due to the ulterior decomposition of the dibromophenol, thus: $2C_6H_3Br_2 \cdot OH = C_6H_2Br_3 \cdot OH + C_6H_4Br \cdot OH$.

V. H. V.

Formation of Phenylglyoxylic Acid from Benzoic Cyanide. By K. Buchka (*Ber.*, **20**, 395—398).—The author has repeated his former experiments (this Journal, 1877, ii, 485) on the action of hydrochloric acid on an acetic solution of benzoic cyanide. He finds that his phenoxylic acid is identical with Claisen's phenylglyoxylic acid, the melting point given (*loc. cit.*) being due to an admixture of

benzoic acid. Besides this acid, its α-amide, $Ph{\cdot}CO{\cdot}CONH_2$, and the so-called γ-amide, $(C_8H_7NO_2)_2$, are produced, as well as the compound $C_{16}H_{12}N_2O_3$ previously described (*loc. cit.*). The latter compound is probably somewhat analogous in formation and constitution to the nitrile described in the Abstract, p. 483. It is very stable towards acids, alkalis, and reducing and oxidising agents, and is now being investigated. The phenylglyoxylic acid is probably formed from the α-amide, and not from the compound $C_{16}H_{12}N_2O_3$. L. T. T.

Methyl Salt of Methyldibromoparacoumaric Acid. By A. Valentini (*Gazzetta*, **16**, 424—425).—The methyl salt of paramethoxycoumaric acid, $OMe{\cdot}C_6H_4{\cdot}C_2H_2{\cdot}COOMe$, crystallises in laminæ melting at 89°; when dissolved in chloroform it readily takes up a molecule of bromine to form a compound, $OMe{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}COOMe$, which may be regarded as a dibromo-derivative of methylhydroparacoumaric acid. This substance melts at 118°, and forms minute white crystals. V. H. V.

Oxidation of α- and β-Hydropiperic Acids. By C. Regel (*Ber.*, **20**, 414—425).—By the oxidation of the α-acid in alkaline solution by very dilute potassium permanganate, *hydroxypiperohydrolactone*, $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3{\cdot}CH_2{\cdot}CH<\begin{matrix}CH(OH){\cdot}CH_2\\O\text{———}CO\end{matrix}>$, and small quantities of piperonal, piperonylic acid, and oxalic acid are produced. This lactone crystallises in long, glistening, colourless needles, soluble in water, ether, and chloroform, insoluble in light petroleum. It melts at 104·5°. Bromine acts on it readily, hydrogen bromide being evolved and a bromo-derivative formed; this crystallises in needles. When the lactone is dissolved in a small quantity of warm concentrated potash, and the product cooled in a freezing mixture and treated with a very slight excess of sulphuric acid, *β-γ-dihydroxypiperohydronic acid*, $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, separates. This acid forms minute white crystals melting at 123°, at the same time giving off water and re-forming the lactone. When an aqueous solution of the acid is boiled, it is partially converted into the lactone, but, on the other hand, an aqueous solution of the lactone is by long-continued boiling partially converted into the acid. The addition of a few drops of hydrochloric or sulphuric acid facilitates the conversion of the acid into the lactone, and even determines it in the cold. The *barium salt* is soluble in water, the *silver salt* sparingly so.

When β-hydropiperic acid is similarly treated with permanganate, it yields, besides piperonal and oxalic acid, methylenehydrocaffeic (piperopropionic) acid, $CH_2:O_2:C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ (Lorenz, Abstr., 1881, 49), and *α-β-dihydroxypiperohydronic acid*,

$$CH_2:O_2:C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH.$$

The latter is easily soluble in alcohol and boiling water, sparingly so in benzene, carbon bisulphide, chloroform, light petroleum, and cold water. It crystallises in colourless, concentrically grouped

needles, and melts at 165°. Its *calcium salt* (+ H_2O) and *silver salt* are sparingly soluble. It does not form a lactone.

The oxidation of the hydropiperic acids appears to take place by the addition of oxygen and the elements of water to the two doubly-linked carbon-atoms. The non-formation of a lactone and the production of methylenecaffeic acid from the β-acid leaves little doubt that the formula for β-hydropiperic acid is

$$CH_2:O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot CH:CH\cdot COOH,$$

and of the dihydroxy-acid that given above. The formation of a lactone from the α-acid proves that one of the doubly-linked carbon-atoms must be in the γ-position to the carboxyl-group, but whether the second occupies the β- or δ-position is still uncertain. The author believes the former probably to be the case when the formula $CH_2:O_2:C_6H_3\cdot CH_2\cdot CH:CH\cdot CH_2\cdot COOH$, given by Fittig to α-hydropiperic acid, would be the correct one, and those of its derivatives would be those given above. L. T. T.

Action of Bibasic Acids on Thiocarbimides. By F. Moinè (*Chem. Centr.*, 1887, 39—40).—When equal molecules of phthalic acid and allylthiocarbimide are heated together at 145°, allylphthalimide is formed; when treated with bromine in carbon bisulphide solution, it yields the dibromide melting at 108—109°.

Allylsuccinimide, $C_2H_4<^{CO}_{CO}>N\cdot C_3H_5$, is obtained by heating together equivalent amounts of succinic acid and allylthiocarbimide. It is a mobile, colourless, not unpleasant smelling oil, boiling at 244—245°; sp. gr. = 1·1543 at 0°, 1·1432 at 12°, 1·1112 at 50°, and 1·0677 at 100°, compared with water at 4°. It is easily soluble in water, alcohol, and ether, has a neutral reaction, is decomposed on boiling, and gives a semi-solid compound with bromine.

Phenylsuccinimide, $C_2H_4<^{CO}_{CO}>NPh$, is obtained by heating succinic acid and phenylthiocarbimide at 140°; it melts at 253—255°. There is also formed a little *succinanilide*, $C_2H_4(CONHPh)_2$. Malonic acid and phenylthiocarbimide yield malondianilide (Abstr., 1884, 729).

Allylcamphorimide, $C_8H_4<^{CO}_{CO}>N\cdot C_3H_5$, is formed when camphoric acid is heated with allylthiocarbimide. It forms colourless plates, and melts at 48—49°. It is almost insoluble in water, soluble in alcohol and ether.

When the anhydrides of phthalic and camphoric acids are heated with allylthiocarbimide, the corresponding imides are formed, together with the above compounds. G. H. M.

Action of Phenylhydrazine on Lactones. By W. Wislicenus (*Ber.*, **20**, 401—403).—V. Meyer and Münchmeyer have shown (Abstr., 1886, 883) that phthalide reacts with phenylhydrazine to form a nitrogenous compound. The author has investigated this reaction, and finds the compound formed to be a simple additive pro-

duct, $C_{14}H_{14}N_2O_2$, and not a substance, $C_{14}H_{12}N_2O$, formed by the elimination of water (*loc. cit.*). The compound $C_{14}H_{14}N_2O_2$ crystallises in minute, glistening needles, easily soluble in boiling alcohol, insoluble in water and benzene. It melts at 173—174° with partial decomposition into its constituents. It is very unstable towards dilute acids and alkalis, thus differing from the hydrazine condensation products of the aldehydes and ketones. It dissolves to a colourless solution in strong sulphuric acid, but the addition of a trace of an oxidising agent such as ferric chloride produces a reddish-violet coloration. Bulow has observed a similar reaction with the acid hydrazides, and the author considers that the constitution of the compound is probably $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO{\cdot}N_2H_2Ph$.

Valerolactone reacts with phenylhydrazine in an exactly similar manner, producing a compound which crystallises in small flat needles. It seems to have the formula $C_{11}H_{16}N_2O_2$, and the melting point 76—79°, but the author has not yet succeeded in obtaining it in a pure state. It is soluble in alcohol, benzene, chloroform, and water, insoluble in ether. L. T. T.

Nitrobenzyl-derivatives of Ethyl Malonate. By E. Lellmann and C. Schleich (*Ber.*, **20**, 434—442).—In the reaction between paranitrobenzyl chloride and ethyl sodiomalonate there are formed simultaneously ethyl mono- and di-nitrobenzylmalonate, of which the latter, $C(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2(COOEt)_2$, crystallises in silky needles melting at 170°, sparingly soluble in alcohol, chloroform, and benzene; the former, $CH(CH_2{\cdot}C_6H_4{\cdot}NO_2)(COOEt)_2$, crystallises in golden-green prisms. On treatment with alkali, the di-derivative is unaltered, whilst the mono-derivative is converted into paranitrobenzylmalonic acid, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(COOH)_2$, a light yellow powder, which carbonises at 240° without fusion. An ammoniacal solution of this acid gives precipitates with solutions of salts of the heavy metals. The above di-derivative when reduced gives an amido-derivative, $C(CH_2{\cdot}C_6H_4{\cdot}NH_2)_2(COOEt)_2$, a hard crystalline mass, the platinochloride of which crystallises in leaflets, the sulphate and the oxalate in scales. In a similar manner *ethyl nitrobenzylethylmalonate*, $CEt(CH_2{\cdot}C_6H_4{\cdot}NO_2)(COOEt)_2$, is produced from paranitrobenzylic chloride and sodium ethylmalonate; this crystallises in colourless needles, melts at 52°, and is soluble in alcohol, ether, and benzene. On treatment with potash and subsequent acidification, this compound is converted into *paranitrobenzylethylacetic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHEt{\cdot}COOH,$$

a sparingly soluble substance, carbonising at 300° without fusion.

Similarly from ethyl sodiomalonate and orthonitrobenzylic chloride the corresponding ortho-compound, $C(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2(COOEt)_2$, is produced, which forms golden crystals melting at 97°, soluble in alcohol and ether. Ethyl orthonitrobenzylethylmalonate was not obtained in a definite state; on hydrogenation, the impure product is converted into ethyl β-ethylhydrocarbostyril-β-carbonate,

$$<\begin{matrix}C_6H_4{\cdot}CH_2\\NH—CO\end{matrix}>CEt{\cdot}COOEt,$$

which crystallises in colourless silky needles melting at 114°. Similar experiments on the reduction of ethyl orthodinitrobenzylmalonate led to indefinite results. V. H. V.

Synthesis of the Ethereal Salts of Trimesic Acid. By A. Piutti (*Ber.*, **20**, 537—539; *Chem. Centr.*, 1887, 36—37).—*Ethyl trimesate*, $C_6H_3(COOEt)_3$, is formed when 16 grams of sodium are added to 72 grams (1 mol.) of ethyl formate and 86 grams (1 mol.) of ethyl acetate in the cold and the mixture then heated, but by acting on a mixture of ethyl acetate and formic acid with sodium, ethyl formylacetate is not formed but only ethyl acetoacetate. The author considers that the ethereal salt of trimesic acid is formed by the condensation of three molecules of ethyl formylacetate with elimination of three molecules of water. When sodium acts on a mixture of methyl formate with ethyl acetate or of ethyl formate with methyl acetate in molecular proportions, a mixture of methyl and ethyl trimesates is formed in each case. The reaction takes place much more readily when a mixture of the two radicles is used than when one radicle only is present.

Methyl trimesate, $C_6H_3(COOMe)_3$, crystallises from dilute alcohol in small needles and melts at 143°.

When ethyl formate is added to a solution of sodium in ethyl acetate, it is decomposed into alcoholate and carbonic anhydride.

G. H. M.

The Six Isomeric Toluenedisulphonic Acids. By P. Klason (*Ber.*, **20**, 350—357).—Toluenedisulphonic acid, [Me : $(SO_3H)_2$ = 1 : 2 : 6], was prepared by Komatzki (Abstr., 1884, 70). The constitution ascribed to it by the author is shown by the fact that it is formed from parabromotoluene (hence neither sulphonic group can have the para-position), and by its non-identity with the three acids which are shown to have a sulphonic group in the meta-position.

Toluenorthometadisulphonic acid, [Me : $(SO_3H)_2$ = 1 : 2 : 3] (this vol., p. 264), was obtained by Limpricht and Richter (Abstr., 1885, 1233) from paratoluidine, and by the author (*loc. cit.*) from toluenemetasulphonic acid.

Tolueneorthometadisulphonic acid [1 : 2 : 5] was first obtained by Håkansson (*Ber.*, **5**, 1088), who named it β-toluenedisulphonic acid. It was prepared by the author (*loc. cit.*) by heating toluenemonosulphonic acid with fuming sulphuric acid at 180°. When orthotoluidine is heated with sulphuric acid, orthotoluidinemetasulphonic acid [1 : 2 : 5] (Nevile and Winther, Trans., 1882, 421) is formed. Orthotoluidinemetasulphonic acid was converted into the diazo-compound, and the latter, after being carefully dried (it explodes easily), gradually added to a warm alcoholic solution of potassium sulphide. The product is diluted with water and treated with lead acetate, filtered and treated with ammoniacal solution of lead acetate; the precipitate is washed and decomposed by hydrogen sulphide. The impure orthothiocresolmetasulphonic acid [1 : 2 : 5] is oxidised by potassium permanganate, the tolueneorthometadisulphonic acid thus formed treated with phosphoric chloride, and the acid chloride converted into the corresponding acid by heating it with water at 140°.

The acid thus obtained is identical with β-toluenedisulphonic acid, and has the constitution [1 : 2 : 5].

Toluneorthoparadisulphonic acid [1 : 2 : 4] is the α-toluenedisulphonic acid prepared by Blomstrand (*Ber.*, **4**, 717); it was also prepared by Senhofer (*Annalen*, **164**, 129), who described it as γ-toluenedisulphonic acid, supposing it to be different from the α-acid, and by Håkansson (*loc. cit.*). It is formed both from tolueneparasulphonic acid (Fahlberg, Abstr., 1879, 804) and from tolueneorthosulphonic acid (Klason and Berg, Abstr., 1880, 889), and has, therefore, the constitution given by the author.

Toluenemetadisulphonic acid [1 : 3 : 5] was prepared by Limpricht and Hasse (*Ber.*, **18**, 2177). Orthotoluidinemetasulphonic acid was converted into orthotoluidinedisulphonic acid, which has the constitution [1 : 2 : 3 : 5] (Nevile and Winther, *loc. cit.*). This was converted by means of the diazo-compound into the iodotoluenedisulphonic acid, from which the iodine was eliminated by boiling with strong hydrochloric acid.

Toluenemetaparadisulphonic acid [1 : 3 : 4] is prepared in the following manner:—Paratoluidinemetasulphonic acid is converted into a toluidinedisulphonic acid. The latter is converted into the diazo-compound, which is converted successively into parathiocresolmetasulphonic acid and toluenedisulphonic acid. The potassium salt of the acid is treated with phosphoric chloride, and the chloride, after being recrystallised from chloroform several times, is converted into the acid by heating it with water at 140°. Like all toluenedisulphonic acids, it is extremely soluble in water. The *potassium salt* (with 1 mol. H_2O) crystallises in needles and is readily soluble; the *barium salt* (with 2 mols. H_2O) forms lustrous prisms soluble in 666 parts of cold water. The *chloride*, $C_7H_6(SO_2Cl)_2$, melts at 111°, and dissolves readily in chloroform, less in ether. The *amide* melts at 235—239° with slight decomposition; it dissolves readily in water and alcohol.

Dithiocresolsulphonic acid, $S(C_7H_6{\cdot}SO_2{\cdot}OH)_2$, was obtained in small quantity; the *chloride* melts at 192°, and is very sparingly soluble in all solvents except glacial acetic acid. N. H. M.

Diphenylhydroxyethylamine. By H. Goldschmidt and N. Polonowska (*Ber.*, **20**, 492—495).—When benzoïnoxime is reduced with sodium amalgam and acetic acid (compare this vol., p. 249), diphenylhydroxyethylamine, $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NH_2$, is obtained; it crystallises in small, white, transparent needles, melts at 161°, and is insoluble in water, sparingly soluble in ether and cold alcohol. The *hydrochloride*, $C_{14}H_{15}NO,HCl$, crystallises in long needles, melts at 210° with decomposition, and is readily soluble in water; the *platinochloride*, $(C_{14}H_{15}NO)_2,H_2PtCl_6 + 2H_2O$, forms microscopic, golden-yellow scales; the *acetate* crystallises in prisms showing a vitreous lustre and melts at 156°. By the action of acetic anhydride on the base, a *diacetyl*-derivative is obtained; it is a white crystalline powder, melts at 159°, and is soluble in benzene. Diphenylhydroxyethylamine, when heated with methyl iodide, yields a tertiary base, $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NMe_2$; this crystallises in long, white needles, melts at 108—110° and forms a *platinochloride*, $(C_{16}H_{19}NO)_2,H_2PtCl_6 + \frac{1}{2}H_2O$. W. P. W.

Condensation-derivatives of Ethylenediamine. By A. T. Mason (*Ber.*, **20**, 267—277).—In a previous communication (Abstr., 1886, 329), the author described a condensation product of ethylenediamine and phenanthraquinone, to which he now assigns the name

$$\begin{matrix} C_6H_4\cdot C\cdot N\cdot CH_2 \\ | \quad \| \quad | \quad | \\ C_6H_4\cdot C\cdot N\cdot CH_2 \end{matrix}$$

xenylenedihydropyrazine, . Its basic powers are very feeble, the hydrochloride even decomposing in dry air; the platinochloride, $(C_{16}H_{12}N_2)_2,H_2PtCl_6$, crystallises in small, slender, pale-yellow needles. It is not decomposed when heated with concentrated hydrochloric acid, even at 230°.

Diphenyldihydropyrazine, $C_4N_2H_4Ph_2$, is prepared by heating equimolecular proportions of benzil and ethylenediamine in alcoholic solution in a reflux apparatus for ½ hour. It crystallises in pale-yellow prisms, melts at 160—161°, is sparingly soluble in cold, readily in hot alcohol, in ether and benzene, and is insoluble in water. It is insoluble in cold mineral acids, but is decomposed by them into its components on warming. When hydrogen chloride is passed into its solution in benzene or ether, ethylenediamine hydrochloride separates whilst benzil remains in solution. This ready decomposibility points to its constitution being dissimilar to that of the stable xenylenedihydropyrazine; it is probably represented by $<\begin{matrix}CPh:N\cdot CH_2\\CPh:N\cdot CH_2\end{matrix}>$.

Ethylenediamine reacts readily with aldehydes with formation of condensation products which, like that last described, are but little stable towards acids.

Dibenzylidenethylenediamine, $C_2H_4(N:CHPh)$, is prepared by mixing ethylenediamine (1 mol.) and benzaldehyde (2 mols.), when considerable evolution of heat occurs; the reaction is completed by heating for half an hour at 120°. It crystallises in large, colourless tables, melts at 53—54°, is insoluble in water, and readily soluble in alcohol and benzene. Dilute acids reconvert it into its components. It is quickly decomposed by boiling with water, or even by exposure to moist air.

Diisopropylbenzylidenemethylenediamine, $C_2H_4(N:CH\cdot C_6H_4Pr)_2$, is obtained by heating cuminaldehyde and ethylenediamine for about a quarter of an hour at 120°. It crystallises in long, pale-yellow needles, melts at 63—64°, is readily soluble in ether, alcohol, benzene, chloroform, and light petroleum, and resembles the preceding compound in its behaviour with water and acids.

Diphenylallidenethylenediamine, $C_2H_4(N:CH\cdot CH:CHPh)_2$, is obtained by mixing cinnamaldehyde with ethylenediamine, external heating being unnecessary; it forms large, colourless tables, melts at 109—110°, is but moderately soluble in ether, readily in alcohol and benzene. When treated with acids, cinnamaldehyde separates.

Diorthohydroxybenzylidenethylenediamine, $C_2H_4(N:CH\cdot C_6H_4\cdot OH)$, prepared by boiling salicylaldehyde and ethylenediamine in alcoholic solution, crystallises in large, yellow tables, melts at 125—126°, is sparingly soluble in cold alcohol or ether, readily in hot, or in benzene. Cold dilute acids do not seem to act on it, but on heating it is resolved into its components.

Diorthomethoxybenzylidenethylenediamine, $C_2H_4(N:CH\cdot C_6H_4\cdot OMe)$,

prepared from methylsalicylaldehyde, crystallises in colourless rhombohedrons, melts at about 113°, and is sparingly soluble in ether, readily in alcohol and benzene. The corresponding para-compound, prepared from anisaldehyde and ethylenediamine, forms large pale-yellow tables, melts at 110—111°, and is sparingly soluble in cold benzene, readily in ether or alcohol. Both compounds are readily decomposed by acids.

Dimethylbenzylidenethylenediamine, $C_2H_4(N : CMePh)_2$, is prepared by mixing phenyl methyl ketone with ethylenediamine and completing the reaction by heating for a short time at 120°. It crystallises in white needles, softens at 95°, melts at 103—105°, is sparingly soluble in ether, readily in alcohol and benzene; it is very readily reconverted into the ketone and amine.

Ethyl ethylenedi-β-amido-α-crotonate, $C_2H_4(NH{\cdot}CMe : CH{\cdot}COOEt)_2$, is obtained by mixing ethylenediamine and ethyl acetoacetate together with a little water or, better, by employing alcoholic solutions of the two substances. It crystallises in large, well-formed prisms, melts at 126—127°; is decomposed on distillation with formation of a basic substance, and is insoluble in water, very sparingly soluble in light petroleum, sparingly in cold but readily in hot alcohol, ether, and benzene. The *free acid* is obtained by heating the ethyl salt with water, or the formation and hydrolysis of the ethyl salt may be combined by heating ethylenediamine and ethyl acetoacetate in sealed tubes at 120—140°. It forms white scales of silky lustre, melts at 167—168°, is readily soluble in water, sparingly in ether, benzene, and cold alcohol, does not show any reaction to litmus-paper, and in aqueous solution gives an intense violet coloration with ferric chloride. Much ethylenediamidopropylene is formed at the same time as the acid. A. J. G.

Condensation of Aldehydes with Phenols and Aromatic Amines. By L. Claisen (*Annalen*, **237**, 261—274).—The action of benzaldehyde on β-naphthol has been described by Trzcinski (Abstr., 1884, 1185) and also by the author (this vol., p. 270). The product, benzal dinaphthal oxide, cannot be directly prepared by the action of β-dinaphthyl oxide on benzaldehyde.

Ethylidene dinaphthyl acetal and ethylidene β-dinaphthyl oxide have been previously described by the author (*loc. cit.*).

Benzaldehyde unites with β-naphthylamine, forming *benzal-β-naphthylamine*, $Ph{\cdot}CH : N{\cdot}C_{10}H_7$, a crystalline compound soluble in chloroform. It melts at 102—103°. At a higher temperature, and under suitable conditions, the aldehyde and amine condense, forming phenylhydronaphthacridine. This substance is insoluble in alcohol. On oxidation, it yields phenyl-β-naphthacridine (m. p. 294), which has been described by Claus and Richter (Abstr., 1884, 1358).

W. C. W.

Action of Chlorine on Aceto-α-naphthalide. By P. T. Cleve (*Ber.*, **20**, 448—451).—When chlorine is passed into a solution of acet-α-naphthalide in acetic acid, crystals of a *dichloro-derivative*, $C_{10}H_5Cl_2{\cdot}NHAc$, separate out; this compound melts at 214°, is readily soluble in acetic acid, alcohol, and chloroform. When boiled with

concentrated potash, it yields *dichloronaphthylamine*, $C_{10}H_5Cl_2{\cdot}NH_2$, melting at 82°, soluble in alcohol, volatile in steam; it yields phthalic acid when heated with nitric acid. By the diazo-reaction, the amine is converted into *dichloronaphthalene*, crystallising in needles which melt at 60°; on oxidation, it yields phthalic acid. It has been shown by Claus that β_1-β_2-dichloronaphthalene melts at 60°, whereas the author has obtained a dichloronaphthalene of the same melting point from two isomeric nitronaphthalene-β-sulphonic acids; hence there are either two isomeric dichloronaphthalenes of the same melting point or an isomeric transformation occurs. If the above dichloroacetnaphthalide is treated with tin and hydrochloric acid, a tin salt, $C_{10}H_6Cl{\cdot}NH_2,HSnCl_3$, separates, from which *monochloronaphthylamine* may be obtained; this crystallises in white needles, melting at 56°, and is sparingly soluble in boiling water, soluble in alcohol. Its *hydrochloride* and *sulphate* crystallise with 1 mol. H_2O in delicate white needles. It is not identical with the monochloronaphthylamine prepared by Atterberg. V. H. V.

Naphthoxyacetic Acids. By M. Spica (*Gazzetta*, **16**, 437—445). —The α- and β-naphthoxyacetic acids are readily obtained by heating monochloracetic acid with the corresponding naphthol in equimolecular proportions, and gradually adding potash solution; the product is most conveniently purified by acidifying the crude product and separating the unaltered naphthol by solution in ammonium carbonate.

α-Naphthoxyacetic acid crystallises in small prisms of pale-rose tint, soluble in ether and alcohol, sparingly soluble in water. It melts at 190°, and is slightly altered by light, especially when moist. The *ammonium* salt crystallises in stellate groups of needles or scales, soluble in water, more so in alcohol; it melts at 119—120°; the *potassium* salt with $1H_2O$ forms long silky needles: the *magnesium* with $6{\cdot}5H_2O$ crystallises in rose-coloured laminæ; the *lead* salt and the *barium* salt with $4{\cdot}5H_2O$ in sparingly soluble laminæ. The *ethyl* salt crystallises in small colourless crystals, soluble in alcohol and ether, melting at 173—174°, and the *amide* in colourless needles, sparingly soluble, and melting at 155°.

The corresponding β-acid crystallises in the trimetric system, and is coloured an azure-green tint on exposure to light; it melts at 151—152°. Its *ammonium* and *potassium* salts crystallise in white micaceous scales, the *barium* salt with $3{\cdot}5H_2O$ in laminæ; whilst the *lead* salt is a white, sparingly soluble crystalline powder. The *ethyl* salt crystallises in large, transparent scales, melting at 48—49°, and the amide in long tablets, melting at 147°, very soluble in alcohol and ether.

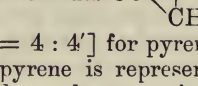
The above acids are isomeric with the naphthylglycollic acid, of which the α-modification has been described. V. H. V.

Constitution of Acenaphthene and of Naphthalic Acid. By E. Bamberger and M. Philip (*Ber.*, **20**, 237—244).—Naphthalic acid, obtained from acenaphthene by oxidation, has been generally regarded as a 1 : 2 derivative of naphthalene, inasmuch as it yields an anhydride and an imide—properties characteristic of the ortho-position in the benzene molecule. Starting, however, from 1 : 1′ nitro-

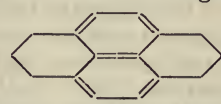
naphthoic acid (melting at 215°), the authors have effected the synthesis of naphthalic acid, and hence have proved that both it and acenaphthene are 1 : 1′ derivatives of naphthalene; this fact, taken in conjunction with Ekstrand's observation (Abstr., 1886, 155) that 1 : 1′ nitronaphthoic acid when reduced yields an amido-acid which undergoes spontaneous conversion into naphthostyril (an "internal" anhydride), and the fact that 1 : 1′ diamidonaphthalene reacts with benzaldehyde as though it were an orthodiamine, proves that in naphthalene the position 1 : 1′ functions as an ortho-position, and renders inevitable an extension of our conception of the latter in hydrocarbons built up of two or more benzene nuclei. The authors propose to distinguish the 1 : 1′ position in naphthalene by the prefix "peri," and term naphthalic acid, for example, perinaphthalenedicarboxylic acid.

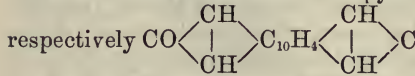
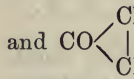
To obtain naphthalic acid, the hydrochloride of the amido-acid prepared from naphthostyril by boiling it with aqueous soda and adding hydrochloric acid to the cold solution was converted into cyanonaphthoic acid by diazotising, and from it, by hydrolysis with aqueous potash, an acid was obtained which agreed with naphthalic acid in all its properties.

α-Naphthamide, $C_{10}H_7{\cdot}CONH_2$, crystallises in large, white, monoclinic tables, showing a satiny lustre, and melting at 202°. W. P. W.

Pyrene. By E. Bamberger and M. Philip (*Ber.*, **20**, 365—371; compare Abstr., 1886, 718, 948, this vol., p. 271).—The formation of naphthalenetetracarboxylic acid by the oxidation of pyrenic acid shows that the latter has the constitution $C_{10}H_4(C_2H_2CO)(COOH)_2$. The positions of the four carboxyl-groups in naphthalenetetracarboxylic acid, which are shown to be [1 : 4 : 1′ : 4′], point to the further developed constitutional formula  [$C_2H_2{\cdot}CO$ = 1 : 1′ and $(COOH)_2$ = 4 : 4′] for pyrenic acid.

The constitution of pyrene is represented by a combination of a naphthalene nucleus with two benzene-rings thus:—



The constitutional formulæ of pyrene quinone and pyrene ketone are respectively  [CH : CH = 1 : 1′ and 4 : 4′] and  .

N. H. M.

Derivatives of Camphoroxime. By H. Goldschmidt (*Ber.*, **20**, 483—485).—A reply to Leuckart (this vol., p. 376) in which the author maintains the correctness of his formulæ for camphoroxime-derivatives. Calcium campholenate by dry distillation yields a hydro-

carbon boiling chiefly between 130° and 140°; an imperfect analysis points to the formula C_9H_{16}, and the compound is possibly identical with campholene. W. P. W.

Naringin. By W. Will (*Ber.*, **20**, 294—304).—Methylnaringenic acid (Abstr., 1885, 906), when oxidised, yields anisaldehyde and anisic acid: the conclusion that this leads to, that methylnaringenic acid is paramethylcoumaric acid, and that naringenic acid is paracoumaric acid was at once confirmed by a comparison of these various acids and their derivatives. As previously shown (*loc. cit.*), naringenin yields phloroglucinol and "naringenic acid" when heated with aqueous potash, it must therefore be *phloroglucinolparacoumarate*,

$$OH\cdot C_6H_4\cdot CH : CH\cdot COO\cdot C_6H_3(OH)_2,$$

naringin being a compound of this substance with isodulcitol.

Naringin in aqueous solution has a rotatory power $[\alpha]_D = -84{\cdot}5$, in alcoholic solution the rotation is stronger, $[\alpha]_D = -87{\cdot}6$.

A. J. G.

Substances Extracted from the Illicium Religiosum. By J. T. Eijkman (*Rec. Trav. Chem.*, **5**, 299—304; compare Abstr., 1886, 95).—From various portions and especially from the fruit of the species of the *illicium* genus, the author has extracted an acid, $C_7H_{10}O_5$, soluble in alcohol and ether, insoluble in chloroform and benzene. It is proposed to designate this substance *shikimic acid*. On distillation, it is for the most part decomposed into phenol and carbonic anhydride, but small quantities of protocatechuic acid are obtained; this acid is also present in the above-mentioned plants.

Shikimic acid is thus probably an additive product of protocatechuic acid, $C_6H_6(OH)_3\cdot COOH$, and is thus analogous to quinic acid, with whose anhydride it is isomeric. The specific rotatory power of the acid in aqueous solution is $[\alpha]_D = -179{\cdot}3$; it shows some slight aptitude for etherification. The ammonium salt crystallises well, and on dry distillation yields a basic substance which gives precipitates with the reagents for the alkaloïds. V. H. V.

Andromedotoxim. By H. G. de Zaaijer (*Rec. Trav. Chim.*, **5**, 313—322).—*Andromedotoxim*, a toxical substance, present in various species of the *Andromeda*, was first isolated by Plugge; it can also be extracted from the *Rhododendron ponticum* by infusion with water, concentration of the extract, precipitation of the albuminous substances with basic acetate of lead, and evaporation of the filtrate. It is best purified from accompanying impurities by frequent recrystallisations from chloroform and ether. Thus obtained, it crystallises in long needles, melts at 228°, is more soluble in cold water than in hot, soluble in alcohol. Its specific rotatory power in aqueous solution is $-9{\cdot}7$, in alcohol $= -14$, but in chloroform is $+10$ to $+12$. Its composition is $C_{31}H_{51}O_{10}$; thus it appears not to be identical with asbetoxime. In its chemical properties it is neither acidic nor basic, and is not of the nature of a glucoside; it does not reduce silver salts, and gives no precipitate with the salts of the heavy metals and the reagents for the alkaloïds. Heated with dilute sulphuric acid, it gives

a rose-red and, with hydrochloric acid, a pale-yellow coloration. It acts as a powerful poison, diminishing the rate of respiration, and producing paralysis; in these effects, it surpasses apomorphine.

V. H. V.

Crystalline Compound from "Kamala." By L. Jawein (*Ber.*, **20**, 182—183).—Andersen obtained (*Jahresber.*, 1855, 669) from kamala a compound which he described as rottlerin, $C_{11}H_{10}O_3$. The author, by extracting kamala with carbon bisulphide or benzene, obtained a yellow crystalline substance melting at 200°. It resembles Andersen's compound in its solubility and in giving a red liquid with alkali, but the analytical results do not agree with the formula suggested by Andersen. (Compare A. G. Perkin and W. H. Perkin, this vol., p. 272.)

N. H. M.

Algaborilla. By G. H. Hurst (*Dingl. polyt. J.*, **262**, 288).—This yellow dye is a species of tannin obtained from the pods yielded by two plants, namely, *Prosopis pallida* and *P. algarobo*, which are indigenous in the mountainous regions of South America. 52 to 55 per cent. of the pods consist of soluble matter containing 27—29 per cent. of tannin. Algaborilla forms yellow precipitates with the salts of zinc, antimony, lead, or aluminium, and imparts to cotton or wool mordanted with metallic salts a yellow colour which bears light very well, and resists weak acids. Alkalis change the colour to brown.

D. B.

Indian-yellow and Glycuronic Acid. By E. Külz (*Zeit. Biol.*, **23**, 475—485).—Baeyer (*Annalen*, **155**, 257) showed that euxanthic acid, which is combined with magnesia in the purree of commerce, can be decomposed by heating with hydrochloric acid, thus: $C_{19}H_{16}O_{10} + H_2O = C_{13}H_8O_4 + C_6H_{10}O_7$; that is, two substances, euxanthone and an acid which was shown by Spiegel (Abstr., 1883, 219) to be glycuronic acid. From glycuronic acid a crystalline anhydride ($C_6H_8O_6$) can be obtained. From the glycuronic acid, obtained from purree, an anhydride with the same formula is also obtainable. The melting point is 160°, when the heat is gradually applied; 170—180° when it is rapidly applied. Its specific rotation is $(\alpha)_D = +19{\cdot}4$.

Euxanthone was obtained free from glycuronic acid by crystallising out the anhydride; it was obtained free from the remainder of the euxanthic acid by treating with ether in which euxanthone is readily soluble. The statement of text-books that euxanthic acid is readily soluble in ether is an error. The separation may also be performed by treating with benzene.

A rabbit was fed on 0·7 gram of euxanthone; the urine was collected, evaporated to a small bulk, and hydrochloric acid added. After standing, a deposit of yellow needles was formed which were dissolved in alcohol and then recrystallised; they consisted of euxanthic acid. In order to settle the question whether purree is of animal or vegetable origin, urea, uric acid, and hippuric acid were sought for in it with positive results.

Purree is stated by some to be a deposit in the urine of camels if they eat the fruit of the *Garcinia mangostana*, from which Schmid separated the principle *mangostin*. When, however, rabbits are fed

upon the fruit or on mangostin, no euxanthic acid appears in the urine.

Schmiedeberg and Meyer regard the glycuronic acid as formed from the grape-sugar in the body. But if its formula, its optical properties, and its reduction power be considered, it is possible that it may have its origin in inosite. W. D. H.

Pyrrolidine. By A. Ladenburg (*Ber.*, **20**, 442—444).—Pyrrolidine is formed in small quantities during reduction of ethylene cyanide (Abstr., 1886, 528); the base is more conveniently prepared by the dry distillation of tetramethylenediamine hydrochloride. It boils at 85—88°, and fumes in the air when slightly warmed. The *platinochloride* forms orange-yellow crystals, and the *bismuthoiodide*, $3C_4H_9NHI,2BiI_3$, red prisms. V. H. V.

Preparation of Pyridine Bases. By E. Dürkopf (*Ber.*, **20**, 444).—The aldehyde-ammonias, when heated with the aldehydes, yield bases of the pyridine series; thus collidine is formed from ethaldehyde and its ammonia compound. It appears probable that the ketones also undergo a similar change. V. H. V.

Lutidines of Coal-tar. By G. Lunge and J. Rosenberg (*Ber.*, **20**, 127—137).—The sulphuric acid used in purifying coal-oil was diluted with 3 or 4 times the volume of water, left for several days and filtered. The filtrate was evaporated, treated with aqueous soda, and the oil so obtained separated and steam-distilled. It was then dried by means of caustic alkali and fractionally distilled. 20 litres of sulphuric acid yielded 800 grams of mixed bases. The fraction boiling at 141—144° yielded by precipitation with mercuric chloride (Ladenburg and Roth, Abstr., 1885, 557) the mercuriochloride of lutidine, from which the pure base was separated and identified. The fraction boiling at 153—156° yielded α-γ-lutidine; this was converted by oxidation into α-lutidinic acid. When the fraction boiling below 170° was oxidised with potassium permanganate, α-lutidinic and isocinchomeronic acids were obtained. The formation of the latter acid points to the presence of α-β-lutidine in the mixed bases. The acid was separated by the method of Weidel and Herzig (*Wien. Akad. Ber.*, **80**, 821). N. H. M.

Ethoxylutidine. By F. Canzoneri and G. Spica (*Gazzetta*, **16**, 449—453).—When ethyl acetoacetate is heated with excess of ammoniacal zinc chloride in sealed tubes at 100—110°, an ethoxylutidine is formed along with other products, and a considerable quantity of carbonic anhydride is evolved; the reaction is as follows:—$2COMe{\cdot}CH_2{\cdot}COOEt + NH_3 = C_5NH_2Me_2{\cdot}OEt + CO_2 + EtOH + 2H_2O$. This compound is a pale-yellow liquid boiling at 245—247°, and resembling pyridine in odour.

On repetition of former experiments (Abstr., 1885, 751) on the condensation of ethyl acetoacetate and formamide, an ethyl monolutidinecarboxylate was obtained as a transparent, yellow liquid of peculiar odour, boiling at 250—255°; this compound appears to be

isomeric with the ethyl monolutidinecarboxylate obtained by Michael from aldehyde, aldehyde ammonia, and ethyl acetoacetate (Abstr., 1885, 1244). V. H. V.

Action of Ammonia and of Primary Amines on Ethyl Dimethylpyronedicarboxylate. By M. Conrad and M. Guthzeit (*Ber.*, **20**, 154—162).—*Ethyl acetyllutidonecarboxylate*,

$$CO<\begin{matrix}C(COOEt):CMe\\C(COOEt):CMe\end{matrix}>NAc,$$

is obtained by heating ethyl lutidonecarboxylate (Abstr., 1886, 334) with an excess of acetic anhydride at 140—150°. It dissolves readily in ether and in boiling alcohol; it melts at 65°.

Lutidonecarboxylic acid, $CO<\begin{matrix}C(COOH):CMe\\C(COOH):CMe\end{matrix}>NH$, separates from its aqueous solution in prisms which melt at 267° with evolution of carbonic anhydride. It is very sparingly soluble in hot water, alcohol, and ether. The *calcium salt* (with 2 mols. H_2O) is readily soluble in hot water; the *copper salt* (with $1\frac{1}{2}$ mol. H_2O) and other salts were prepared.

Lutidone (2, 6-dimethylpyridine), $CO<\begin{matrix}CH:CMe\\CH:CMe\end{matrix}>NH$, is formed when the carboxylic acid is heated at 270—290° until no more carbonic anhydride is given off; it is best purified by distillation. It is very readily soluble in water and alcohol, almost insoluble in ether, benzene, and chloroform. It separates from the aqueous solution in lustrous, monoclinic needles (with 3 mols. H_2O); $a:b:c = 1{\cdot}1396:1:2{\cdot}6179$; $\beta = 85{\cdot}11°$. The anhydrous substance melts at 225° and boils at 349—351°. It gives a brown-red coloration with ferric chloride. It is identical with the compound obtained by Haitinger from dehydracetic acid (Abstr., 1885, 761). The *platinochloride*, $(C_7H_9NO)_2,H_2PtCl_6$, forms microscopic, transparent plates which melt at 224—225°. The *chromate* crystallises in well-formed, yellowish-red prisms, readily soluble in water, sparingly in alcohol. It melts at 125° with decomposition. The *picrate* crystallises in slender needles melting at 219—220°.

Ethyl methyllutidonedicarboxylate, $CO<\begin{matrix}C(COOEt):CMe\\C(COOEt):CMe\end{matrix}>NMe$, is formed when solutions of ethyl dimethylpyronedicarboxylate and methylamine in acetic acid are mixed. It crystallises in rosettes of needles melting at 193°. The *free acid* melts at 255°, and at the same time decomposes into carbonic anhydride and *methyllutidone*. The latter crystallises in long, lustrous needles which melt at 110—111°; it dissolves readily in alcohol and water.

Phenyllutidonedicarboxylic acid, $CO<\begin{matrix}C(COOH):CMe\\C(COOH):CMe\end{matrix}>NPh$, is prepared by the hydrolysis of the ethyl salt (Abstr., 1886, 334). It crystallises in prisms readily soluble in boiling alcohol, sparingly in ether, benzene, and water. The *hydrogen barium salt*, $(C_{15}H_{12}NO_5)_2Ba + H_2O$, is readily soluble; other salts were prepared.

Phenyllutidonemonocarboxylic acid, $CMe\langle^{NPh\cdot CMe}_{CH-CO-}\rangle C\cdot COOH$, is obtained by heating the dicarboxylic acid at 227°. It crystallises in long, lustrous needles which melt at 257°; it dissolves in hot water and alcohol.

Phenyllutidone, $CO\langle^{CH:CMe}_{CH:CMe}\rangle NPh$, is prepared by heating phenyllutidonedicarboxylic acid at 270°. It is identical with the compound obtained by Perkin from aniline and dehydracetic acid (Abstr., 1885, 762). N. H. M.

Lutidine-derivatives from Lutidinedicarboxylic Acid. By M. Conrad and W. Epstein (*Ber.*, **20**, 162—166).—When lutidone is distilled with zinc-dust, lutidine is formed. It boils at 144—145°, and is identical with that obtained by Epstein (Abstr., 1886, 257) from 2, 6-dimethylpyridinetricarboxylic acid.

Chlorolutidinedicarboxylic acid, $CCl\langle^{C(COOH)\cdot CMe}_{C(COOH)\cdot CMe}\rangle N$, is prepared by heating lutidonedicarboxylic acid with three times its weight of phosphorus pentachloride and some phosphorus oxychloride at 140°. The oxychloride is then mostly distilled off, the residue treated with water, filtered, and evaporated. It crystallises from water in white prisms which become brown at 217° and melt at 224°.

Chlorolutidine, C_7NH_8Cl, is obtained by heating dry lutidone (20 grams) with phosphoric chloride (35 grams), and some phosphorus oxychloride at 140°. It is purified by steam distilling. It is a clear colourless oil having an odour resembling that of lutidine; it boils at 178°; sp. gr. at 17° = 1·105. The *hydrochloride* forms slender needles. The *platinochloride* and *mercurichloride* melt at 225° and 155° respectively. Chlorolutidine suspended in water gives with picric acid a yellow compound melting at 150—156°. The *chromate* forms orange-coloured crystals which blacken at 140°. *Ethoxylutidine*, obtained by heating chlorolutidine with alcoholic solution of sodium ethoxide, is a colourless oil boiling at 217°.

Phenylamidolutidine, $C_5NH_2Me_2\cdot NHPh$ [Me : NH : Me = 2 : 4 : 6], is formed when chlorolutidine and aniline are heated at 195° for one hour. It melts at 150°, and boils at 335—338°, and dissolves readily in alcohol, ether, and dilute acids. When treated with sulphuric acid, and then with a trace of nitric acid, it gives a blood-red coloration, which disappears on adding water or more nitric acid. The *platinochloride* forms slender needles which melt at 209°.

N. H. M.

Condensation Product of Ethyl Amidoacetoacetate with Hydrochloric Acid. By N. Collie (*Ber.*, **20**, 445—447).—In a former paper it has been shown that ethylic amidoacetate yields pyridine-derivatives on condensation (Abstr., 1885, 373). If hydrogen chloride is passed into an ethereal solution of this substance an additive compound, $C_6H_{11}NO_2,HCl$, is produced, which forms deliquescent crystals, and is decomposed in aqueous solution into ethyl acetoacetate and ammonium chloride, but when heated by itself it

yields a substance, $C_{10}H_{13}NO_3$, isomeric with the ethyl salt of a hydroxylutidinecarboxylic acid, melting at 137°, and showing remarkable stability towards reagents. On treatment with concentrated potash, and acidification of the product, an acid, $C_8H_9NO_3$, is formed; this is an insoluble crystalline powder which melts at 300°, with evolution of carbonic anhydride and distillation of a white crystalline substance, C_7H_9NO, which melts at 176°, and boils without decomposition at 306·5°. From these properties, it is probably identical with pseudolutidinecarbostyril. In like manner ethyl amidoacetoacetate hydrochloride when heated with 1 mol. of the amido-acid itself yields ethyl pseudolutidostyrilcarboxylate, from which the carbostyril is obtained by hydrolysis. V. H. V.

Ethyl Dimethylpyronedicarboxylate. By M. Conrad and M. Guthzeit (*Ber.*, **20**, 151—154).—Ethyl 2, 6-dimethyl-3, 5-pyronedicarboxylate, $C_{15}H_{16}O_6$ (Abstr., 1886, 333), melts at 80°. When 1 gram of the ether is boiled with aqueous baryta, acetone (0·08 gram), barium malonate (0·17 gram), and barium acetate are formed; no oxalate is produced. This decomposition corresponds with that of dehydracetic acid, which was shown by Oppenheim and Precht (*Ber.*, **9**, 323) to be decomposed by bases into acetone, acetic acid, and carbonic anhydride. Wislicenus (*Ber. chem. Gesell. Würzburg*, **17**, 16) found that malonic acid is also formed in larger or smaller amount, in the decomposition of dehydracetic acid, according to the strength of the baryta solution. N. H. M.

Quinoline. By E. Lellmann and H. Alt (*Annalen*, **237**, 307—327).—1, 4-*Dimethylquinoline*, $C_9NH_5Me_2$, prepared by the action of sulphuric acid on a mixture of paraxylidine sulphate, nitrobenzene, and glycerol. The product is poured into water, and the excess of nitrobenzene removed by distillation in a current of steam. The base is liberated by the addition of an alkali, and distilled in a current of steam. It is a liquid boiling at 265° under 736 mm. pressure. It solidifies in a freezing mixture, forming colourless crystals which melt between 4° and 5°. The sp. gr. of the liquid is 1·070 at 21°. The *dichromate*, $(C_{11}H_{11}N)_2,H_2Cr_2O_7$, melts at 149°, and crystallises in orange-coloured needles. The platinochloride forms anhydrous needles. When oxidised with nitric acid (22 per cent.) at 170°, the base is converted into 1, 4-*methylquinolinecarboxylic acid*, $C_9NH_5Me{\cdot}COOH$. This acid melts at 286°. The *hydrochloride*, $C_{11}H_9O_2N,HCl + H_2O$, forms silky needles, which are decomposed by water. The *platinochloride* contains 6 mols. H_2O.

The ammonium salt gives a crystalline precipitate with calcium chloride, and amorphous precipitates with ferrous sulphate, lead acetate, and copper salts. The methylquinoline which is produced when this acid is heated with lime is identical with the methylquinoline from orthotoluidine.

1, 4-*Bromoquinolinecarboxylic acid*, $C_9NH_5Br{\cdot}COOH$, is prepared by heating at 160° a mixture of parabromometamidobenzoic acid, orthonitrophenol, glycerol, and sulphuric acid. The product is mixed with water, and the excess of nitrophenol distilled off in a current of steam.

Baryta is added to the residue, the precipitated barium sulphate removed by filtration, and the excess of baryta precipitated by carbonic anhydride. On acidifying the filtrate with acetic acid, bromoquinolinecarboxylic acid is deposited as a white powder. The pure acid melts at 275°. It is insoluble in water, but dissolves in boiling alcohol and in hot acetic acid. The ammonium salt yields crystalline precipitates with barium and calcium chlorides, and with potassium dichromate, and amorphous precipitates with lead acetate and mercuric chloride.

The platinochloride, $(C_{10}H_6O_2NBr)_2,H_2PtCl_6 + 4H_2O$, is crystalline. Reduction with tin and hydrochloric acid converts bromoquinolinecarboxylic acid into *tetrahydroquinolineanacarboxylic acid*,

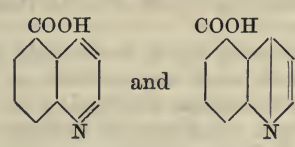
$$C_9NH_{10}\cdot COOH\ [COOH = 4];$$

this forms colourless needles, and melts at 146—147°. The *hydrochloride*, $C_{10}H_{11}O_2N,HCl + H_2O$, crystallises in colourless needles. The *nitrosamine* is deposited from alcohol in yellow prisms, which melt at 186° with decomposition. This tetrahydro-derivative is identical with the tetrahydroquinolinecarboxylic acid described by Fischer and Körner (Abstr., 1884, 1197).

Skraup and Brunner (Abstr., 1886, 811) have recently shown that the carboxyl in quinolinecarboxylic acid from metamidobenzoic acid (which is identical with Fischer's acid) occupies the 4 (ana) position.

The quinolinecarboxylic acid which the authors prepared from metamidobenzoic acid differed in many of its properties from the acid which Skraup obtained from the same source. The chief points of difference are as follows :—The acid melts at 338°. The hydrochloride, $C_{10}H_7O_2N,HCl$, crystallises in colourless needles or prisms containing 1 mol. H_2O. The aqueous solution of the ammonium salt gives with lead acetate a white precipitate *insoluble* in acetic acid, no precipitate with nickel sulphate, and a pale blue precipitate with copper salts, soluble in excess of the reagent on boiling, and crystallising out on cooling.

Both quinolinecarboxylic acids yield the same tetrahydro-derivative. The following formulæ are proposed for these isomerides.



W. C. W.

Synthesis of Metaquinolinecarboxylic Acid. By M. Tortelli (*Gazzetta*, **16**, 366).—When a mixture of the stannochloride of amidophthalic acid, $C_8H_5(NH_2)O_4,HSnCl_3 + 2H_2O$, and nitronaphthalic acid is heated with glycerol and sulphuric acid, as in Skraup's reaction, it yields a mixture of quinoline- mono- and di-carboxylic acids; these may be separated by repeated sublimation, the latter being gradually converted into the former with elimination of the carbonic anhydride. The monocarboxylic acid crystallises in minute needles which melt at 248·5—250°; it is insoluble in ether, almost insoluble in benzene and cold water, readily soluble in alcohol. Its solutions give various

precipitates with ferrous and ferric, copper, silver, cobalt, and nickel salts. This acid is identical with one recently obtained by Skraup from metamidobenzoic acid (this vol., p. 160). V. H. V.

α-Alkylcinchonic Acids. By O. Doebner (*Ber.*, **20**, 277—281). The author explains the formation of aniluvitonic acid (2′ : 4′ methylquinolinecarboxylic acid) from aniline and pyruvic acid by assuming that acetaldehyde is intermediately formed by the splitting up of a molecule of pyruvic acid, and then condenses with aniline and a second molecule of pyruvic acid after the manner of the quinaldine synthesis. The correctness of this assumption has been proved by preparing the whole series of α-alkylcinchonic acids by the action on aniline of a mixture of pyruvic acid with the homologues of acetaldehyde, the reaction being expressed by the general equation $R\cdot CHO + CMeO\cdot COOH + C_6H_5\cdot NH_2 = C_6H_4<^{-N\,:\,CR-}_{C(COOH)}>CH + 2H_2O + H_2$. These acids, on distillation with lime, are readily converted into the α-alkylquinolines. A more detailed description of these substances will be given later.

If an aldehyde and aniline in alcoholic or ethereal solution are allowed to react with pyruvic acid in the cold, neutral crystalline compounds are formed, which are not related to the quinoline series, and from which aniline can again be readily obtained; these will be described later. If, on the other hand, the mixture in alcoholic solution is heated for four hours on the water-bath in a reflux apparatus, then the α-alkylcinchonic acids are formed and in part separate on cooling, in part are obtained on evaporating the solution. They are readily purified by crystallisation from acetic acid or alcohol.

α-Ethylcinchonic acid, $C_9NH_5Et\cdot COOH$ [2′ : 4′], prepared from propaldehyde, pyruvic acid, and aniline, crystallises in colourless plates, melts at 173°, and is soluble in both acids and alkalis. The silver salt, $C_{12}H_{10}NO_2Ag$, forms white plates soluble in water. *α-Ethylquinoline*, C_9NH_6Et [Et = 2′], prepared by distilling the acid with soda-lime, is a colourless oil of quinaldine-like odour, and boils at 245—246°. The platinochloride, $(C_{11}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in orange-red needles.

α-Isopropylcinchonic acid, $C_9NH_5Pr^{\beta}\cdot COOH$ [2′ : 4′], obtained from isobutaldehyde, pyruvic acid, and aniline, in well-formed crystals, melts at 146°. When heated with soda-lime, it yields *α-isopropylquinoline*, $C_9NH_6Pr^{\beta}$, a colourless oil boiling at 255°; the platinochloride, $(C_{12}H_{13}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles.

α-Isobutylcinchonic acid, $C_4H_9{}^{\beta}\cdot C_9NH_5\cdot COOH$ [2′ : 4′], prepared from isovaleraldehyde, pyruvic acid, and aniline, crystallises in silky, white plates, melting at 186°. When distilled with soda-lime it gives *α-isobutylquinoline*, $C_9NH_6\cdot C_4H_9$, as a colourless oily liquid of peculiar odour, boiling at 270—271°. The platinochloride forms large, orange-red, anhydrous needles.

α-Phenylcinchonic acid, $C_9NH_5Ph\cdot COOH$ [2′ : 4′], prepared as above from benzaldehyde, crystallises in colourless needles, melts at 202—203°, forms a platinochloride crystallising in orange-red needles, and when distilled with soda-lime yields the known α-phenylquinoline.

A. J. G.

Isoquinoline and its Derivatives. By S. Hoogewerff and W. A. Van Dorp (*Rec. Trav. Chim.*, **5**, 305—312).—Isoquinoline, isolated from coal-tar, can be regarded as a β-derivative of naphthalene. It is best obtained in a state of purity by recrystallising its sulphate from alcohol until the melting point of the salt (205°) is constant; the free base melts at 22° and boils at 240—245°. It forms crystalline combinations with various metallic salts, and unites with the alkyl iodides, to form replaced ammonium iodides such as isoquinoline-methylammonium iodide, C_9H_7N,MeI, crystallising in plates melting at 158—161°, and the corresponding ethyl compound, C_9H_7N,EtI, which crystallises in tables melting at 147°. The substances are distinguished from similar derivatives of quinoline in not forming cyanines.

Isoquinoline yields a sulphonic acid, the barium salt,

$$(C_9H_6NSO_3)_2Ba,9H_2O,$$

of which crystallises in needles. On hydrogenation, the base yields a tetrahydro-additive product, $C_9H_{11}N$, a liquid boiling at 232°, and not solidifying at −15°; it absorbs carbonic anhydride to form a crystalline carbonate; a hydrochloride, crystallising in small tables melting at 232°, and a platinochloride in reddish-yellow tables, were also obtained. It seems that these quinoline-derivatives are of therapeutic value.

V. H. V.

Acid Morphine Meconate. By D. B. Dott (*Pharm. J. Trans.* [3], **17**, 690).—The author has not succeeded in preparing and identifying morphine hydrogen meconate.

Constitution of Brucine. By A. Hanssen (*Ber.*, **20**, 451—460).—With the view of throwing further light upon the constitution of brucine, the preparation and composition of kakotheline, originally obtained by Strecker, have been further investigated. To this substance is ascribed the formula $C_{21}H_{22}N_4O_9$, instead of $C_{20}H_{22}N_4O_9$, hitherto accepted. When reduced, it yields a base, the analysis of whose hydrochloride pointed to a formula $C_{21}H_{25}N_3O_5$, derived from kakotheline by the reduction of one nitro-group and elimination of another. With bromine, kakotheline yields an acid substance, $C_{19}H_{24}N_2O_7$, the platinochloride of which crystallises in orange-yellow needles, its silver salt in glistening needles; its methyl salt could not, however, be obtained, but the crude product treated with ammonium chloride yielded a base, $C_{19}H_{22}Me_2N_2O_7$, crystallising in yellow, sparingly soluble prisms. In this reaction, the acid seems to be analogous to nicotinic acid, and thus it would appear that in kakotheline, as also in brucine, a pyridine grouping is present. The above acid when oxidised with chromic acid yields the base $C_{16}H_{18}N_2O_4$, obtained formerly as a product of decomposition of brucine. According to the author there is present in brucine, besides a quinoline-group, also a dimethoxyphenylpyridine, and in strychnine, a phenylpyridine residue; the stability of brucine seems to indicate a ring-arrangement.

V. H. V.

Hydrastine. By J. F. Eijkman (*Rec. Trav. Chim.*, **5**, 290—298).—Mahla, Power, and more recently Freund and Will (this vol., p. 174),

have examined hydrastine, a principle obtained from the *Hydrastis canadensis*. The formula assigned to this substance by these chemists is $C_{22}H_{23}NO_6$, that of the author is more in accordance with the formula $C_{21}H_{21}NO_6$, and the results are also confirmed by analysis of the auro- and platino-chlorides, as also of the sulphate. The specific rotatory power is $[\alpha]_D = -66{\cdot}3$, $l = 200$, in chloroform solution, a value practically equal to that of Freund and Will. On decomposition with nitric acid, it yields opianic acid and a 12-carbon nitrogeneous compound, a result more simply explained by the above formula, thus: $C_{21}H_{21}NO_6 + H_2O + O = C_{11}H_{13}NO_3 + C_{10}H_{10}O_5$. V. H. V.

Note.—Freund and Will, in a more recent communication than that referred to above, have independently shown the formula to be $C_{21}H_{21}NO_6$ (see this vol., p. 383). A. J. G.

Optical Behaviour of Cocaïne. Method for Determining the Purity of Cocaïne Hydrochloride. By O. Antrick (*Ber.*, **20**, 310—322).—Analyses of cocaïne hydrochloride pointed to Lossen's formula, $C_{12}H_{21}NO_4,HCl$. Solutions of cocaïne are lævorotatory. Determinations of the specific rotatory power of cocaïne hydrochloride from different sources in dilute alcoholic solution lead to the equations $[\alpha]_D = 52{\cdot}180 + 0{\cdot}1588 \times q$ (q = solvent) and $[\alpha]_D = 67{\cdot}982 - 0{\cdot}15827 \times c$ (c = concentration of solution). When $q = 0$ $[\alpha]_D = 52{\cdot}180$; when $q = 100$ $[\alpha]_D = 68{\cdot}060$. To determine the purity of a preparation, the angle is measured at which the plane of polarised light is turned by the solution. A solution is conveniently used in which 100 c.c. (at 20°) contain 10 or 20 grams of dry cocaïne salt to be tested. A 10 per cent. solution should give (with a tube 200 mm. long) at 20° an angle 13·280°; a 20 per cent. solution an angle 25·927°. When with a 10 per cent. solution the angle is between 13·25° and 13·31°, and with a 20 per cent. solution between 25·90° and 25·96°, the sample is pure. Free cocaïne melts at 98°. The solution in chloroform at 20° has the specific rotatory power $[\alpha]_D = 15{\cdot}827 + 0{\cdot}005848 \times q$. When $q = 0$ $[\alpha]_D = -15{\cdot}827$.

N. H. M.

Action of Pepsin on Amyloïd. By S. Kostiurina (*Chem. Centr.*, 1887, 120).—Working with pure amyloïd, the author found, contrary to the usual statements, that it was soluble in pepsin solution acidified with hydrochloric acid. The probable cause of the mistake is that the organs containing amyloïd have not been divided sufficiently fine before being examined. In order to prepare the amyloïd, the diseased organ was cut in small pieces, the blood washed out with water, then boiled with water, alcohol, and ether, and the purified product submitted to the action of pepsin. After acting on diseased liver so purified with pepsin for 48 hours, a residue remained with the properties of amyloïd; this, when finely powdered and again submitted to the action of a strong digestive solution at 40—50° for 48 hours, was almost entirely dissolved, only a very slight residue of nucleïn and tissue remaining. A similar result was obtained with finely chopped diseased spleen. G. H. M.

Vegetable Globulins. By S. H. C. Martin (*Proc. Physiol. Soc.*, 1887, 8—9).—Vegetable globulins can be divided into two classes, namely, vegetable myosins and vegetable paraglobulins. The myosins, obtained from the flours of wheat, rye, and barley, have similar properties; they are all readily soluble in 10—15 per cent. sodium chloride solution, and are precipitable from this solution by saturation with sodium chloride or magnesium sulphate. They are soluble in 10 per cent. magnesium sulphate solution, and are coagulated in this solution at a temperature of 55—60°. If the salt is dialysed away from the saline solution of myosins, the latter is precipitated; but the precipitate is no longer a globulin, since it is insoluble in saline solutions. It is soluble in dilute acid and alkalis (0·2 per cent.); it is precipitable from these solutions by neutralisation, the precipitate being soluble in excess of alkali or acid; that is, the myosin has been converted into a proteïd, having the properties of an albuminate. If the saline solution of myosin be placed in an incubator at a temperature of 35—40°, in 12 to 18 hours a fine flocculent precipitate falls, while the globulin disappears from the solution; this takes place more rapidly if the saline solution is diluted. The precipitate exhibits the same properties as the precipitate of the globulin by dialysis; that is, at a temperature of 35—40° the globulin is transformed into an albuminate. The ready transformation of the soluble globulin of wheaten flour into an insoluble albuminate is one of the phenomena which takes place during the formation of gluten (Abstr., 1886, 1065).

The second class of vegetable globulins, the paraglobulins, is in distinct contrast with that of the myosins. Two proteïds of this class have been found, one in papaw juice (Abstr., 1886, 642), the other in the seeds of *Abrus precatorius* (jequirity). Both these globulins exhibit the following properties: they are soluble in saline solutions, and are precipitated by saturation with sodium chloride and magnesium sulphate. In a 10 per cent. solution of magnesium sulphate, they coagulate between 70° and 75°. When precipitated from their saline solutions by dialysis, they are still soluble in solutions of sodium chloride and magnesium sulphate of 10—15 per cent., not being transformed into albuminates. Nor are they precipitated by long exposure (over three days) to a temperature of 35—40°.

W. D. H.

Physiological Chemistry.

Estimation of the Carbonic Anhydride Expired, and the Oxygen Absorbed in Respiration. By M. Hanriot and C. Richet (*Compt. rend.*, **104**, 435—437).—The inspired air passes through a meter, and the expired air passes through two meters, between which is the apparatus for absorbing the carbonic anhydride. The difference between the readings of the first and third meter gives the volume of oxygen absorbed, and the difference between the second and third

gives the volume of carbonic anhydride produced. The carbonic anhydride is absorbed in a large tube filled with broken glass, kept moistened by a solution of potassium hydroxide falling from the top. The meters are constructed on the principle of an ordinary gas-meter, and give very accurate measurements. Special arrangements are made to neutralise the effects of the rapid and considerable variations in pressure which take place during the vigorous respiration. A number of test experiments show that the apparatus gives very accurate results. C. H. B.

Formation of Lactic Acid during Muscular Activity, and its Fate in the Organism. By W. Marceuse (*Bied. Centr.*, 1887, 92—94).—The author draws the following conclusions from his researches :—Sarcolatic acid is formed during muscular activity. In the frog, by far the greater part of the lactic acid so formed is destroyed in the liver; but a small portion passes into the urine. During activity, the urine of mammalia is free from lactic acid.

A. J. G.

Formation of Methæmoglobin in Blood by the Action of Alloxantin. By N. Kowalewsky (*Chem. Centr.*, 1887, 164).—Defibrinated blood is changed in colour to brown and then to black by the addition of alloxantin. The absorption-bands of oxyhæmoglobin disappear, and a new band appears in the red, which points to the probable formation of methæmoglobin. When ammonium sulphide is added and the liquid examined spectroscopically, the result shows that methæmoglobin is undoubtedly formed when alloxantin is added to oxyhæmoglobin. Since alloxantin possesses reducing power, this is a new example of the formation of methæmoglobin by reduction. The action of alloxantin does not, however, stop at the formation of this substance, but by further reduction hæmoglobin, and finally an undetermined brown substance, is formed. G. H. M.

Decomposition of Bromides and Iodides by the Stomach. By E. Külz (*Zeit. Biol.*, **23**, 460—474).—Maly (*Sitzungsb. d. K. Akad. d. Wissensch.*, **76**), has shown that free hydrochloric acid is produced by the action of sodium and calcium chlorides on sodium dihydrogen phosphate and disodium hydrogen phosphate, but whether this reaction between the salts of the blood will account for the presence of free hydrochloric acid in the stomach is doubtful. The absence of the acid in the stomach of animals after a fast of 24 hours, and also in new-born animals, places some difficulty in the way of accepting the theory, as it cannot be supposed that diffusion processes stop, or that the salts disappear from the blood. It was thought interesting, therefore, to investigate the question whether the administration of bromides and iodides caused the appearance in the stomach of hydrobromic and hydriodic acids respectively.

As a preliminary investigation, it was found that by distilling bromide of potassium or sodium with hydrochloric acid, no trace of bromine was found in the distillate, whilst minimal quantities of hydrobromic acid added to hydrochloric acid could be detected without difficulty. The method adopted for detecting the acids in the stomach was a

modification of Rabuteau's (*Compt. rend.*, **80**, 61). The gastric juice was collected, in a dog which had fasted 24 hours, by washing out the stomach with distilled water until the washings gave no acid reaction, allowing 200 c.c. of distilled water to remain in the stomach 30—40 minutes, and then withdrawing it. This turned methylaniline-violet blue; it was digested with freshly precipitated quinine at 60°, and evaporated to a thick syrup which crystallised on cooling. This was dried over sulphuric acid and powdered and shaken up with pure chloroform.

The dried chloroform residue was divided into two parts, in one portion the ash, and in the other the chloride (as silver chloride) was estimated. Lactic acid was in all cases absent. The next question was whether this method would avail to detect free hydrobromic or hydriodic acids in the presence of hydrochloric acid and salts of those acids; in artificial mixtures, the silver precipitate consisting of chloride and bromide of silver was obtained by the method just described; the precipitate was weighed, then heated in a tube and a stream of chlorine passed over it; from the loss of weight so produced the amount of bromide in the mixture was calculated. Experiments were then performed in which bromide of sodium, bromide of potassium, and iodide of potassium were respectively given to dogs for several days, the animal was then allowed to fast 24 hours, and the gastric juice collected as described; full details of the analyses are given; they show that after the administration of bromides small quantities of free hydrobromic acid, after the administration of iodides small quantities of free hydriodic acid are present mixed with free hydrochloric acid in each case. W. D. H.

Nutritive Value of Glycerol. By L. Arnschink (*Zeit. Biol.*, **23**, 413—432).—Several previous investigations have been made to determine the influence exerted by glycerol on the metabolism of proteïds; the general results obtained being that small doses produced no alteration, while large doses such as those given by Lewin and Tschirwinsky (Abstr., 1880, 817) produced an increase in the total amount of urine, with a slight rise also in the total amount of urea excreted. From these experiments, glycerol does not seem to effect any saving in the decomposition of proteïds, such as is brought about by other substances free from nitrogen, like fats and carbohydrates. Scheremetjewski (*Arbeit. aus d. physiol. Anstalt, Leipsig*, 1869, 194) found that the injection of 2 grams of glycerol into the blood-vessels of rabbits produced an increase in the amount of carbonic anhydride expired for the space of an hour after the injection.

The present investigation takes into account the output both of nitrogen and carbon; the urine, fæces, expired air, and perspiration, being analysed from a dog who was fed on two occasions each lasting three days, on 50—80 grams of glycerol in addition to 200 grams of meat and water, and these results are compared with those obtained when the dog was fed on meat and water alone. The results relating to the excretion of nitrogen were as follows:—

Day of experiment.	Amount of glycerol.	Daily amount of nitrogen excreted.	
		1st experiment.	2nd experiment.
1, 2	none	6·85 grams	7·47 grams
3, 4	50 grams	7·00 „	7·50 „
5	80 „	7·60 „	8·05 „
6	none	8·16 „	8·89 „
7	none	8·30 „	8·61 „

The increase with the larger dose is seen to be marked (10—20 per cent.), and to last for the two days following its administration. A certain amount of unchanged glycerol was found in the urine, but its amount was not proportional to the amount ingested; it therefore had to be estimated daily. The amount of carbon in the urine during the period when glycerol was given as compared with that when it was not given, showed that the increase during the former period was simply due to the unchanged glycerol present, and not to any other compound containing carbon, the result of its decomposition. The fæces were also examined for unchanged glycerol, and a mere trace (0·53 per cent. of the glycerol ingested) was all that was found.

The next question investigated was the effect of glycerol on the laying on of fat. The following table compares the output of nitrogen and carbon:—

Day.	Nitrogen.	Carbon.			
		Total.	From proteïd.	From glycerol.	From fat.
1	6·72	42·99	22·04	—	20·95
2	6·98	42·15	22·89	—	19·26
3	7·08	45·89	23·22	12·93	9·74
4	6·93	48·28	22·73	11·64	13·91
5	7·60	56·26	24·93	21·15	10·18
6	8·16	47·14	26·76	—	20·38
7	8·30	41·31	27·22	—	14·09

That is to say, the glycerol furnishes a good deal of the carbon, and so economises the amount of fat which undergoes combustion; a similar table was made as the result of a second experiment.

Upon the data that the combustion of 1 gram of the carbon of fat gives rise to 12·35 cal., of glycerol to 11·01 cal., and 1 of the nitrogen of meat to 25·95 cal., other tables to show the heat value of glycerol have been calculated, of which the following is an example:—

Day.	Cal. from N.	Cal. from glycerol.	Cal. from fat.	Total.
1	174·38	—	258·73	433·11
2	181·13	—	237·86	418·99
3	183·73	142·36	130·29	456·38
4	179·83	128·16	169·69	477·68
5	197·22	232·86	124·86	554·94
6	211·75	—	250·70	462·45
7	215·38	—	173·02	388·40

This shows that although the glycerol saves the combustion of fat, yet more than an equivalent amount of glycerol undergoes combustion, giving rise to an unnecessarily large production of heat; the final calculation showing that on the three days of its administration, 21, 41, and 55 per cent. of it respectively underwent combustion over and above that which was necessary to compensate for the fat saved.

W. D. H.

Addition of Sugar to Cattle Foods. By T. Pfeiffer and F. Lehmann (*Bied. Centr.*, 1887, 46—50).—These experiments were made in continuation of those of Henneberg and Holdefleiss (Abstr., 1885, 1252; 1886, 727). Two sheep were fed on different kinds of fodder for certain periods, and afterwards on a mixture containing a considerable proportion of sugar; the proteïn, fat, cellulose, and mineral matters digested were carefully estimated in the usual manner; the conclusion arrived at was that the addition of sugar had no influence on the digestibility of the other substances. J. F.

Wheaten Gluten as a Food. By A. Constantinidi (*Zeit. Biol.*, 23, 433—455).—This research was undertaken first on dogs and then on men, to ascertain the value of wheaten gluten as a food, and consequently its use among the poorer classes on account of its cheapness. The following results were obtained from a three days' experiment on a dog, 100 grams of the gluten with 100 grams of fat being given daily; the intake of nitrogen was 37·44 grams, the output in the urine 35·2 grams, and in the fæces 1·3, a total of 36·5. Moreover, some of the nitrogen in the fæces is doubtless derived from the digestive juices and mucus secreted in the alimentary canal. 3·05 per cent. of the fat given was all that was left undigested. In a second experiment, lasting five days, a gain of nitrogen was also noted, the figures being as follows:—The intake of nitrogen was 123·16 grams; the output 124·27 grams (in the urine 121·01, in the fæces 3·26 grams). The fat given was all absorbed with the exception of 2·8 per cent. of it found in the fæces.

Similar experiments were then performed on the laboratory servant, who had eaten so many kinds of food given him by other experimenters, that he took this artificial mixture with relish. The food given consisted of potatoes, gluten (200 grams daily), lard, beer, common salt and water, all of which were previously analysed. The result of a three days' experiment was as follows:—Intake of nitrogen

95·091 grams; output in urine 72·25, and in fæces 6·07, total 78·32 grams. The amount of nitrogen retained in the body was therefore 16·76. 6·4 per cent. of the nitrogen given was not absorbed from the alimentary canal, and 2·5 per cent. of the fat given also appeared in the fæces; of the starch given only 0·38 per cent. remained unabsorbed; whereas the fæces contained 78 per cent. of the cellulose contained in the food.

A second research, lasting three days, was also performed, and the diet was the same with the exception that no gluten was given, and the result showed that the gain in nitrogen observed in the first experiment was clearly due to the gluten; in this second experiment the intake of nitrogen being 21·522 grams, and the output 28·67 grams (24·47 in the urine, 4·2 in the fæces). The conclusion is drawn that this food is an exceedingly valuable one. W. D. H.

Digestion in the Pig. By Ellenberger and Hofmeister (*Bied. Centr.*, 1886, 833—837).—The pigs, after a hunger period, were fed with oats, and then killed in 1, 2, 3, 6, 8, 10, and 12 hours after feeding. It appeared on examination of the pig that digestion takes place in two or three stages. The first and principal is the amylolytic digestion, when all the starch is rendered soluble in 1—2 hours—simultaneously the lactic fermentation commences when a not inconsiderable quantity of sugar is converted; the formation of methane was not proved. In two hours, 34 per cent. of the insoluble albumin becomes soluble. The mucous membrane of the cardiac sac, where are located peculiar glands, contains a weak diastatic ferment; during the first period the reaction is alkaline for a short period only, and as the acidity which later on appears, is due to lactic acid, the conversion of starch still continues.

The second period, when starch is being converted in the cardiac, and albumin in the pylorus, is of a mixed character, commencing at the third hour, and continuing to the ninth to twelfth. There appeared to be only 60—70 per cent. of water in the stomach.

The stomach is not emptied of food until 24 to 36 hours have elapsed since feeding, even if the food has been easily digestible. The amount of acid present seems to rise gradually from 0·002 per cent. to 0·05 per cent., immediately after feeding; to 0·7 in the cardiac half, and to 0·2 in the pyloric half. As observed in the horse, lactic acid is present at first, then later on hydrochloric acid appears (8—9 hours). E. W. P.

Amido-compounds in the Animal System. By P. Bahlmann (*Bied. Centr.*, 1886, 833).—Asparagine reduces the decomposition of albumin in the bodies of rabbits, sheep, and geese, but appears not to have a like effect in dogs. Tyrosine, taurine, guanidine, and thiocyanates in small doses raise the decomposition of albumin to 168 per cent., as compared with the decomposition occurring in animals fed with non-nitrogenous food; but if leucine be substituted for a part of the asparagine, the great increase is very considerably modified. The nitrogenous compounds in extract of meat neither affect loss of albumin, nor increase the feeding value of non-nitrogenous foods.

E. W. P.

Pepsin versus Animal Digestion. By E. F. Ludd (*Amer. Chem. J.*, **8**, 433—436; compare Abstr., 1886, 646).—It is shown that the artificial pepsin digestion yields results which are practically concordant with those obtained by animal digestion, as given in Kuhn's tables, &c. Armsby's statement that in a fodder over-rich in starch the digestibility of the albuminoïds is decreased, holds in the case of artificial pepsin digestion; and in a compound ration the results are not the same as with each separate component of the ration.

H. B.

Formates in the Organism. By Gréhant and Quinquaud (*Compt. rend.*, **104**, 437—439).—Experiments with dogs show that when sodium formate is introduced into the blood or the digestive canal, the greater part is eliminated in the urine without undergoing any alteration. At the same time, the urine contains no excess of carbonates.

The organic liquid was acidified with sulphuric acid and distilled in a vacuum on a water-bath. The distillate was neutralised, evaporated to a small bulk, and the formate thus obtained was decomposed with strong sulphuric acid, and the volume of evolved carbonic oxide measured. Experiments with an aqueous solution of the formate, and with urine to which a known quantity of formate had been added, gave the necessary correction.

C. H. B.

Reducing Substance in Diabetic Urine. By H. Leo (*Chem. Centr.*, 1887, 193—194).—In addition to dextrose, the author has isolated from diabetic urine a reducing substance which, after being purified from dextrose by repeated treatment with barium hydroxide in methylic alcohol solution, is obtained as a bright-yellow syrup. Its aqueous solution has a strong left-handed rotation, $[\alpha]_D$ being $-26{\cdot}07°$; it is not fermented by yeast, even after being boiled with hydrochloric acid, and it has the composition $C_6H_{12}O_6$. Its reducing power is very much less than that of dextrose. The author suggests that this substance can be determined in diabetic urine by taking the reducing power and optical activity of the urine, removing the dextrose by fermentation, and again determining these constants.

G. H. M.

Creatinine in Urine. By P. Grocco (*Chem. Centr.*, 1887, 17—18).—The author has modified Neubauer's method for the determination of creatinine as follows: During the 24 hours' collection of the sample the urine must be kept acid, if necessary, by the addition of acetic acid, and if possible must be immersed in ice, otherwise a little creatinine may be converted into creatine. An excess of acid is removed by the addition of milk of lime. The urine is then neutralised with lime, calcium chloride added, and the mixture evaporated; the reaction should be either neutral or feebly acid. If the acidity is due to a mineral acid, great care is necessary, and it is advisable to add sodium acetate to the alcoholic extract of the syrupy residue in order to replace it by acetic acid. It is better, however, to entirely dispense with the use of mineral acid and use only acetic acid. The alcoholic solution, to which zinc chloride is to be added, must contain free acetic acid, in order to prevent the precipitation of zinc oxide. On

the other hand too much acetic acid prevents the precipitation of the creatinine zinc chloride. If necessary, the alcoholic extract should be decolorised with animal charcoal before acidification. It is better to cool the solution with ice before adding the zinc chloride. The precipitated creatinine zinc chloride should always be submitted to a microscopic examination with a high power.

With the aid of this method, the author has determined the amount of creatinine in normal and pathological urine. In childhood and old age, human urine contains less creatinine than in middle age. In infants fed with an entire milk diet it does not always occur, but, contrary to Hofmann's statement, it is sometimes found in small quantities during the first months of life. The amount of creatinine increases with a diet of animal food, and decreases on fasting or with a vegetable diet. With increased bodily work, the author found, contrary to Hofmann, that the secretion of creatinine through the kidneys is increased. For the influence of various diseases on the secretion of creatinine in the urine, the original must be consulted.

G. H. M.

Behaviour of Quinol with Urine and Urea. By A. N. Anraeff (*Vrach*, 1887, 230—232).—The author finds that quinol prevents the alkaline fermentation of urine, an addition of 2 per cent. keeping urine without apparent change either to the eye or to test-paper for 25 days. 1 per cent. prevented it from becoming acid or giving off an ammoniacal odour, the reaction being neutral.

Quinol decomposes urea, the solution becoming more and more tawny in colour; the amount of decomposition produced by quinol is proportional to the quantity of urea present. Thus solutions of urea containing 1, 2, and 3 per cent. of urea showed a loss respectively of 1, 0·5, and 0·2 per cent. of the urea present when kept for 24 hours without admixture; solutions of like strength to which 1 per cent. of quinol had been added, showed losses of 17, 19, 15, and 13·25 per cent. of the urea present. It is suggested that quinol acts like acids on urea, decomposing it into ammonia and carbonic anhydride, but at the same time forming a new combination with the former, which is not readily decomposed by sodium hypobromite. This theory would account for the deficiency of nitrogen always observed when solutions of urea containing quinol are analysed.

Quinol was found in the urine by Mering after the administration of arbutin (*Archiv. f. die gesammte Physiol.*, 1877, **62**, 276), and after taking phenol by Baumann and Preusse (Abstr., 1879, 814).

T. M.

Aniline Poisoning. By F. Müller (*Chem. Centr.*, 1887, 193).—Unchanged aniline was found in the urine of a person poisoned with aniline; the urine reduced Fehling's solution, but did not rotate polarised light. Free sulphuric acid was present in small quantity (4·75 mgrms. in 100 c.c.), and combined sulphuric acid in large quantity (76·1 mgrms. in 100 c.c.). A portion of the concentrated urine, when boiled with strong hydrochloric acid, neutralised with sodium hydroxide and extracted with ether, gave an ethereal extract which, when tested, showed the blue indophenol reaction. The ethereal

extract of the unboiled urine did not give this reaction; therefore the aniline must have been secreted as paramidophenyl sulphate. The striking resemblance which patients who have been treated with antifebrin show to persons poisoned with aniline led the author to examine the urine in each case. In both cases methæmoglobin is found in the blood. Aniline does not occur in the urine of patients treated with antifebrin, but by the above treatment it shows the indophenol reaction. Combined sulphuric acid is also present. The author therefore concludes that antifebrin is secreted in the urine in the same form as aniline, that is, as paramidophenyl sulphate. This can be tested for by boiling a little urine with one-fourth its volume of strong hydrochloric acid, adding a few c.c. of a 3 per cent. phenol solution, and then some drops of a chromic acid solution. If paramidophenol is present, the liquid becomes red and changes to blue on addition of ammonia. G. H. M.

Toxic Action of Colchicine. By A. Mairet and Combemale (*Comp. rend.*, **104**, 439—441).—Experiments with dogs and cats show that colchicine behaves as an irritant poison and attacks all the organs, but especially the digestive canal and the kidneys. The action is more rapid when the drug is injected hypodermically than when it is introduced into the stomach. In the first case the minimum fatal dose is 0·000571 gram per kilo. of body-weight; in the second case, 0·00125 per kilo. Details of the symptoms are given in the original paper.

Colchicine is eliminated by various secretions and chiefly in the urine, but the elimination is very slow, and therefore colchicine may behave as a cumulative poison if administered in minute quantities at not too great intervals. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Liberation of Nitrogen from its Compounds, and the Acquisition of Atmospheric Nitrogen by Plants. By W. O. Atwater (*Amer. Chem. J.*, **8**, 398—420; compare Abstr., 1885, 1005, and this vol., p. 292).—The conclusions arrived at are—(1.) During the growth of peas, nitrogen is in most cases acquired from the air, but in some few cases where the conditions of growth are abnormal, there is either no gain in nitrogen or there is a slight loss. This loss is to be explained by the evolution of free nitrogen from the nutriment, or from the seeds and plants during germination and growth; it is probably a constant, and may cause considerable error in all the experiments. (2.) Boussingault has found the amount of atmospheric nitrogen absorbed to be very small, but in his experiments the plants were not normally nourished, and probably, therefore, were less able to resist the action of denitrifying ferments, or to absorb nitrogen from the air. (3.) Numerous experiments have shown a slight gain

or loss of nitrogen during germination and growth, but the failure of an experiment to show the acquisition of nitrogen from the air proves the non-assimilation of atmospheric nitrogen only on condition of the further proof that no nitrogen was liberated, whilst a gain actually observed is positive proof that nitrogen is assimilated either directly by the plants or indirectly through the medium in which the roots developed. (4.) The liberation of nitrogen appears to be due, in some cases, if not in all, to ferments, and it is to be noticed that in nearly all the experiments in which no gain of nitrogen has been observed the plants have been ill fed, or the nutritive solutions have been very concentrated, or other conditions have been abnormal. (5.) The way in which the nitrogen is acquired is still a matter of doubt. (6.) The experiments of Boussingault, and of Lawes, Gilbert, and Pugh which have given the strongest evidence against the fixation of free nitrogen by plants are possibly affected by the loss of nitrogen already referred to, by the exclusion of the action of electricity and of microbes, and by the fact that the plants were also for the most part poorly fed. (7.) In the author's experiments, ignited sea-sand was used for growing the plants in, and hence it is probable that the plants themselves and not the soil are factors in the acquisition of atmospheric nitrogen. (8.) Lawes, Gilbert, and Warington have shown the great probability that the legumes, which appear to possess in high degree the power of obtaining nitrogen from natural sources, induce the action of nitrifying ferments by which the inert nitrogen of the soil is made available. It is equally conceivable that the same plants and others may favour the action of nitrogen-fixing micro-organisms. H. B.

The Functions of Chlorophyll. By A. Nagamatsz (*Chem. Centr.*, 1887, 163—164).—The behaviour of leaves, when immersed in an aqueous solution of carbonic anhydride, depends on whether the water thoroughly wets them, or whether they remain covered by a thin film of air. In the former case no starch is formed, in the latter a great deal.

The slight thickness of the chlorophyll-bearing layer in leaves and other assimilating organs, coupled with the fact that light which has been filtered through a chlorophyll solution possesses in a very slight degree only the power of causing the leaves of aquatic plants to separate oxygen, makes it probable that light, which has passed through an assimilating leaf, no longer possesses the power of causing assimilation in a second leaf. Direct experiments showed that sunlight which had passed through a layer of chlorophyll-containing tissue less than 0·2 mm. thick, was completely deprived of the power of causing assimilation. Etiolated leaves do not possess the power of producing starch. G. H. M.

Influence of Ozone on Germination. By A. Vogel (*Bied. Centr.*, 1887, 142).—Strongly ozonised air seems to have no harmful influence on the germination of seeds. Milk and meat can be kept for a longer time in ozonized air, without change, than in ordinary air. E. W. P.

Formation of Sugar in Grapes. By Müller (*Ann. Agronom.*, **13**, 88—91; from *Bot. Centralbl.*, **27**, 116).—The author gives a *résumé* of some of the principal results of researches on this subject which have been published at the various Conferences of Viticulturists since 1876. The sugar in the grape is a transformation product of starch formed in the leaves, and the green grape itself takes little or no part in its formation; individual grapes of a cluster ripen normally when protected from the light. Assimilation in the grape itself is never active enough to mask respiration. The starch formed in the leaves exposed to light disappears completely when they are placed in darkness for two days. Again placed in the light a new formation of starch can be detected after three-quarters of an hour. 100 grams of leaves (Risling) destroy by respiration alone 3—4 grams sugar in 24 hours. The migration of the reserve materials depends essentially on the temperature; the higher this is the more rapidly do they find their way through the tissues and towards the fruit, the action being most rapid at 30°. The diminution of acidity is not explained by neutralisation of the acid, but by the relation of acid production to respiration. The more energetic the oxidation of the sugar, the more acid will be formed; the acid already formed is further oxidised, ultimately to carbonic anhydride and water. In the ripe grape, the intensity of metamorphosis and the production of acid diminish together.

To ensure the maximum production of sugar, as many leaves as possible must be left on the vine; there is no practical limit to this except the shade produced by too many leaves. The following table shows the effect of leaving 2, 4, 6, or all the leaves on the twig below each bunch of grapes:—

	Weight of grapes.	Quantity of must.	Acid per 1000.	Sugar per cent.	Sugar in kilos.
	kilos.	litres.			
1. Two leaves left....	35·39	22·15	13·6	16·72	3·703
2. Four leaves left....	37·07	22·26	13·5	16·95	3·774
3. Six leaves left	35·02	22·23	15·2	17·36	3·860
4. All leaves left	38·66	24·16	12·2	17·76	4·315

There is thus less sugar and more acid when the leaves are removed. The grapes are less mature, and less lævulose is formed:—

	Dextrose.	Lævulose.
I. Two leaves left.....	8·34	8·38
II. All leaves left.....	8·68	9·18

J. M. H. M.

Presence of Cinnamic Acid in Plants of the Ericaceæ Family. By F. J. Eijkman (*Rec. Trav. Chim.*, **5**. 297—298).—From the leaves of the *Enkianthus Japonicus*, an ornamental plant in Japanese gardens, the author has extracted by means of chloroform a crystalline sub-

stance, proved by analysis and physical properties to be cinnamic acid. V. H. V.

Composition of Lupines. By TROSCHKE (*Bied. Centr.*, 1887, 101—103).—The following tables show the composition of blue, yellow, and white lupines, also of *Lupine cruikshankii* at four different periods of growth, namely: I, when main stems began to bloom; II, main stem in full bloom; III, blooming of side shoots; IV, complete formation of all shoots:—

Period I.

	L. cruikshankii.	Yellow.	White.	Blue.
Ash	6·57	5·92	7·13	7·74
Fibre	26·36	31·51	29·79	26·87
Fat	3·99	3·18	3·06	3·33
Albuminoïds	22·06	17·93	17·79	20·88
Non-nitrogenous extractive	41·02	39·46	38·06	41·18

Period II.

	L. cruikshankii.	Yellow.	White.	Blue.
Ash	5·84	5·81	6·79	6·41
Fibre	28·81	31·10	31·97	30·60
Fat	3·57	3·58	2·94	3·01
Albuminoïds	21·18	18·13	15·79	17·99
Non-nitrogenous extractive	40·60	41·38	42·51	41·99

Period III.

	L. cruikshankii.	Yellow.	White.	Blue.
Ash	5·30	5·87	6·82	6·16
Fibre	38·89	35·51	31·53	31·16
Fat	3·23	2·47	3·22	2·89
Albuminoïds	19·19	19·69	15·01	16·69
Non-nitrogenous extractive	33·59	36·46	43·42	43·10

Period IV.

	L. cruikshankii.	Yellow.	White.	Blue.
Ash	5·04	5·20	5·78	5·38
Fibre	38·95	37·67	37·24	32·62
Fat	3·02	1·77	1·80	2·34
Albuminoïds	18·10	17·15	15·78	16·94
Non-nitrogenous extractive	34·89	38·21	39·40	42·72

The total amount of the ash and albumïnoids as produced by 100 plants shows that the blue lupine is vastly inferior to any of the others, that the white during the first period is the best, but that *L. cruikshankii*, other things considered, is the best, although it is more easily affected by low temperatures. E. W. P.

Composition of the Inner Brown Skin of the Earth-nut. By J. König (*Bied. Centr.*, 1887, 141).—This substance contains water, 9·01 per cent.; albuminoïds, 12·68; fat, 11·76; non-nitrogenous matter, 20·46; fibre, 34·90; ash, 11·19. The author considers the price usually charged for this substance (5·4 marks per centner.) too high; being indigestible, its price ought to be 3 marks.

E. W. P.

Effects of Thiocyanates on Vegetation and Fermentation. By E. Meusel (*Bied. Centr.*, 1887, 66—69).—The presence of thiocyanate in ammonium sulphate has been proved by various observers to be injurious to vegetation, but exhaustive experiments on the subject have not hitherto been made. The author gives the results of his observations.

Seeds lose their power of germination when steeped in a $\frac{1}{2}$ or $\frac{1}{4}$ per cent. solution of ammonium thiocyanate; they rapidly swell, and in the case of wheat the husks burst; the microscopic appearance of the seeds is unaltered. Potassium, ammonium, barium, calcium, and magnesium thiocyanates immediately convert potato and other starches into pastes when preserved in 20 per cent. solutions, the rapidity of action depending on concentration. The paste so produced was almost transparent, similar in appearance to that produced by weak potash solution. Sodium and calcium chlorides, in presence of thiocyanates, yield a starch-paste from which when treated with alcohol a substance, "fraktose," is precipitated, insoluble in water.

The albumin of beet juice is coagulated by thiocyanates, but that of cereals is dissolved; egg albumin is coagulated; blood serum, with 5 to 10 or 15 per cent. solution of ammonium thiocyanate, acquires an acid reaction, and after a time becomes a transparent jelly, which yields a soluble and an insoluble albumin when treated with water. The effect on the skin of animals is to swell them considerably more than other reagents, but to leave the texture unaltered. After a time the skin again contracts, becomes elastic, and resembles india-rubber. This, however, does not occur in acid solutions. J. F.

Grain of Holcus Sorgho. By Bordas (*Compt. rend.*, **104**, 300—302).—Sorghum is now somewhat largely cultivated in the districts of Vaucluse and Le Gard. The grain as ordinarily gathered contains 40 per cent. of starch, and this proportion would in all probability increase to 50 per cent. if the grain were allowed to ripen on the plant. 100 kilos. of grain were found to yield 26 litres of alcohol of 33°, with a good flavour. The hydration of the grain is best effected by the action of diastase, and not by the action of acids, since in the latter case the residue cannot be used as cattle food.

The grain is steeped in water for two or three days to remove the husk, then bruised, treated with the smallest possible quantity of

water, and maintained at 60°, when hydration is soon complete. Hot water is gradually added until the temperature rises to about 70°, the liquid is allowed to stand for two or three hours, and is then treated with beer yeast; when the fermentation is complete, the waste is distilled. C. H. B.

Cider Ash. By G. Lechartier (*Compt. rend.*, **104**, 336—338).—The ash left by cider varies from 1·7 to 4·9 grams per litre according to the district in which the apples are grown. In all cases, from 80 to 92 per cent. of the ash is soluble in water, and the soluble portion consists almost entirely of potassium salts; the potassium doubtless exists in the cider in combination with organic acids. The composition of the ash from one litre of the cider from various districts is given in the following table:—

Insoluble Portion.

	Manche.	Orne.	Eure.	Ille-et-Vilaine.
SiO_2	0·010	0·007	0·007	0·017
P_2O_5	0·039	0·080	0·106	0·081
CaO	0·042	0·074	0·090	0·050
MgO	0·080	0·038	0·089	0·037
Fe_2O_3 and Al_2O_3	0·015	0·013	0·020	0·017
Total	0·186	0·212	0·312	0·202

Soluble Portion.

	Manche.	Orne.	Eure.	Ille-et-Vilaine.
Cl	0·020	0·014	0·006	0·024
SO_3	0·065	0·063	0·050	0·145
P_2O_5	0·117	0·046	0·135	0·149
CO_2	0·397	0·615	0·464	0·289
K_2O	1·113	1·465	1·302	0·970
Na_2O	0·021	0·014	0·018	0·020
Total	1·733	2·217	1·975	1·597

Apples yield from 90 to 95 per cent. of their weight of must, which contains the greater part of the potassium salts existing in the fruit, whilst the greater part of the calcium salts remains behind in the marc.

The quantity of ash obtained from apples themselves varies from 2·105 to 4·47 grams per kilo., but the composition of the ash is always of the same general character, about 80 per cent. being soluble in water. The amount of phosphoric anhydride varies from 7·6 to 16·0 per cent.; of potassium oxide from 44·0 to 58·0 per cent.; of calcium

and magnesium oxides from 7·3 to 14·0 per cent. The presence of a large quantity of calcium compounds in the soil has no sensible effect on the proportion of calcium in the apples, the amount and composition of the ash being practically the same whether the soil is calcareous, granitic, or schistose.

The wood and leaves of the apple tree leave about 2 per cent. of ash, about 50 to 75 per cent. of which is insoluble in water, and consists mainly of calcium and magnesium phosphates and carbonates. The soluble part of the ash contains no phosphoric acid.

C. H. B.

Silage of Maize. By B. Schulze (*Bied. Centr.*, 1887, 96—98). Comparison of the analyses of fresh green maize plants, and of the same when siloed.

Silage of Vegetable Matter. By B. Schulze (*Bied. Centr.*, 1887, 98—101).—With the view of ascertaining the influence of the amount of water present on the quality of silage, hay was wetted with different quantities of water, and then, after fermentation had occurred, analysed. It then appeared, as shown in the tables of analyses given, that the more water there was present the greater was the loss of carbohydrates and crude fibre. The albuminoïds were less altered than was expected, but this the author attributes to the albumin being dry, and therefore less easily attacked by the water. The second set of experiments was undertaken with the object of ascertaining the influence of time on the quality of silage, the examinations being made bimonthly. It appeared that the carbohydrates and cellulose were most affected in the first six months, the loss which occurred in the second half year being much less; the albumins were most affected during the second half year; the ether extractive was gradually and continuously reduced.

E. W. P.

Diffusion Residues. By Märcker (*Bied. Centr.*, 1887, 104—106).—These residues from the sugar factories are treated with milk of lime when being made up into "sections." This process, together with the subsequent pressing, reduces the value of the sections as food, to the extent of 6·12 per cent. dry matter and 5·92 per cent. nitrogen, due in part to compounds found in the liquid which runs from the presses. The amount of lime generally present varies from 1·25 to 4·5 per cent. of the dry matter, and of this 4 per cent. about 2 per cent. is in the form of carbonate; but this large addition of lime to the food of animals (sheep at least) seems to have no harmful influence on them. It is shown that by reason of the neutralisation by the lime of the acids produced during fermentation, they sometimes do not keep as well as if lime were absent. It is advisable, therefore, to dry them in warm chambers, so as to leave only 15 per cent. of water in them.

E. W. P.

Influence of the Physical Properties of a Soil on the Amount of Free Carbonic Anhydride present. By E. Wollny (*Bied. Centr.*, 1886, 806—812).—The soil under examination was placed in wooden boxes 1 metre square and 25 cm. deep, and inclined to the

south at an angle of 10°, 20°, and 30° respectively. An iron tube pierced with holes was sunk in the soil so that the air could be withdrawn by its means. In another series of experiments, like boxes were placed facing the four cardinal points at angles of 15° and 30°. The carbonic anhydride was estimated by Pettenkofer's method. During the three years that these experiments lasted (April—September), it was found that an inclination of 20° was most conducive to the formation of carbonic anhydride, but as the quantity of gas produced was so small, it was decided in 1883 to add 600 grams of horse-dung to the soil, and also to add another set of boxes, in the soil of which grass was sown. The results confirmed those previously obtained, and in addition showed that less carbonic anhydride was evolved from grass-sown soil than from that which was bare. As regards those boxes exposed to the north, south, east, and west, it appears that a southerly exposure produces most decomposition, a northerly least, as warmth and moisture are the factors which regulate decomposition. These experiments further show that a northerly aspect in dry weather is productive of most carbonic anhydride, but in wet weather, when the soil is thoroughly moist, then the south aspect is most effectual in producing decomposition.

It is well known that dark soils are warmer than the lighter coloured, consequently it was to be supposed that the darker soil would produce more carbonic anhydride. In support of this theory, humous calcareous sand was placed in cylinders 0·1 sq. m. diameter, some of the soil being darkened on the surface by powdered coal, whilst the rest was whitened by an admixture of coarsely powdered marble. Contrary to expectation, the dark soil proved poorer in gas than the light. The author explains this result by stating that more water, an important factor of decomposition, was evaporated from the dark soil, consequently in wet weather dark soils would be richest in carbonic anhydride.

The air contained in the ridges of a potato and maize field was found to be poorer in carbonic anhydride than the air drawn from the furrows, because although in the ridge decomposition proceeds more rapidly than in the flat, yet the carbonic anhydride is removed more rapidly by wind and diffusion.

The quantities of carbonic anhydride found in soils containing like amounts of organic matter vary with the coarseness of the grain, the finer the grain the greater the percentage, because the gas can more readily pass out into the atmosphere if produced in a coarse-grained soil.

The percentage of carbonic anhydride increases with depth of soil.

The diffusion of carbonic anhydride through layers of soil of various characters is dependent on the character of the grain, diffusing with the greatest difficulty into the fine-grained earth.

Finally, earth shaded by growing plants (grass) contains less carbonic anhydride during warm weather than bare soil, and this again less than soil which is covered by dead plants (straw); in fact the experiments show that the percentage is trebled by a layer of straw 2·5 cm. thick as compared with grass land; moreover, as the layer of

straw increases, so does the percentage of free gas. The conclusions which may be drawn from these last observations are that the thicker the crop stands on the land the poorer will be that land in free carbonic anhydride, because the temperature and the moisture are lower than those of a bare soil, consequently manures which increase the growth of the crop reduce the percentage of free gas. Further, the amount of gas found in the air of a soil must not be considered as a measure of the intensity of decomposition occurring in soils, nor of the quantity of organic matter present if the surfaces are different.

E. W. P.

Nature of Nitrogenous Organic Matter of Soils. By R. Warington (*Chem. News*, **55**, 27—28).—In the author's experiments, indications of a very small quantity of soluble amide were obtained in the aqueous extract of a soil rich in nitrogen. The soil had been manured annually for the last 38 years with farmyard manure; it contained when dry 0·189 per cent. of nitrogen. The same sample of soil, after treatment with potassium carbonate, yielded an extract which did not contain amide bases or acids soluble in ether, but on treating the acidified extract with phosphotungstic acid it gave a precipitate containing nitrogen (compare Loges, Abstr., 1886, 96). In further experiments it is shown that cold hydrochloric acid removes from both surface- and sub-soils considerable amounts of nitrogenous organic matter, the amount increasing with the strength of the acid and duration of contact. Even when the same soil was treated four times successively there was no apparent exhaustion of this nitrogenous matter. Ammonia was found in the first extracts, but not sought for in the others. The strongest acid employed contained 5 vols. of hydrochloric acid solution per cent. Reference is made to Baumann (this vol., p. 82—84) and to Berthelot and André (*ibid.*, 293—294). The results obtained by Julie (Abstr., 1884, 1413—1416) seem to indicate the synthesis of some such amides as those observed by Berthelot and André (*loc. cit.*). D. A. L.

Decomposition of Organic Matter in Soils. By E. Wollny (*Bied. Centr.*, 1887, 1—11).—The changes which take place during the decomposition of organic matters used as fertilisers, show many points of interest. The fertility of soils depends much on them, and as some of them can be artificially directed, their study is of value.

Carbonic anhydride, water, ammonia, and free nitrogen are disengaged, and where there is free access of air nitric acid is produced, but it has been abundantly proved that nitrification is, partly at least, a physiological process, caused by micro-organisms; little is known of their action, but the presence of oxygen seems to be a necessary condition; the temperature is also an important factor; at 5° nitrification proceeds slowly, at 12° more rapidly, and at 37° it seems to have reached its most favourable stage. Moisture is also an aid to the process, provided it is not so abundant as to stop the pores of the soil and prevent access of air; light is injurious to nitrification, presence of acids stops it, and bases must be present to combine with the nitric acid formed. Soil treated with hydrochloric acid to remove its soluble constituents, yielded very little carbonic anhydride

with organic matter, but when a solution containing those matters was added to it, the production became normal; contrary to general opinion, lime was not found to hasten the decomposition of organic matter; weak solutions of sodium chloride and nitrate were favourable, but strong solutions were not, and the rapidity of decomposition was greatly facilitated by a minute state of division.

A table shows the rate of decomposition of many organic substances, from which it appears that bone meal, fish guano, and birds' excrement are in the first rank, the most difficult being leather and horn meal.

The nitrogen contained in different materials is known to vary in manurial value. The author thinks that which is present in humus and peat is of little worth, and should not add to the value of manure when, in the form of moss litter, it is a constituent of stable manure. The fat contained in certain manure materials aids decomposition; flesh and bone meals deprived of their fat decay more slowly than when it is left in them. J. F.

Behaviour of Urea in Soils. By O. Kellner and others (*Bied. Centr.*, 1880, 812—813).—It is well known that fresh human urine destroys plants, although it is slightly acid, and therefore can be neutralised by the soil, also, that as soon as it has decomposed slightly and become alkaline, it is no longer harmful.

Experiments now prove that it is the urea which is not absorbed by the soil, but coming in contact with roots of plants, prevents absorption of water, and so causes drooping of the leaves. E. W. P.

Manuring with Thomas Slag and other Phosphates. By M. Fleischer, Brinckmann and others (*Bied. Centr.*, 1886, 815—823).—The experiments which are here recorded were made on moorland soils, and with various crops (rye, potatoes, &c.), and all point out the great advantages obtained by the use of Thomas slag; they show that this and precipitated phosphates are equal in gross value, and that Thomas slag is superior in net value; that precipitated iron phosphate is far behind slag on moorlands, and that in those cases where there was no advantage in the first season, the effects showed themselves in the succeeding crop. E. W. P.

Manuring with Thomas Slag. By Fittbogen and Salfeld (*Bied. Centr.*, 1887, 83—88).—Thomas slag, in conjunction with calcium humate and humic acid was employed as a manure in comparison with mono-, di-, tri-, and tetra-calcium phosphates, some of these being assisted by calcium humate; the seed employed was that of barley. The results were unsatisfactory, far less advantage being gained than in the previous year. There seemed to be no relationship between the quantity of manure used and the percentage of ash in the upper portion of the plants; but the percentage of phosphoric acid was increased by the employment of phosphates, and more especially when the calcium humate was added, still more so by the addition of humic acid in the free condition. Salfeld's experiments show that the effect produced by the slag is largely dependent on the character of the soil,

for with him, using nitre and kainite in addition, the results were good. E. W. P.

Manurial Value of Thomas Slag. By P. Wagner (*Bied. Centr.*, 1887, 31—41).—The author has given great attention to the utilisation of this bye-product in agriculture, and has made numerous experiments to ascertain its comparative value as tried against other phosphatic materials.

The composition of the slag explains its ready solubility, the phosphoric acid contained therein being supersaturated with lime, and when put into the soil in a state of fine division, the carbonic anhydride, the humic and other organic acids present readily combine with the lime and set free the phosphoric acid.

Experiments were made at Darmstadt Experimental Station, some in the open field with natural soil, others with the prepared earth in zinc cylinders, loam, calcareous soil, and sand deprived of lime; the plants were oats and barley, the slag being finely ground in some cases, coarse in others; the manure used for comparison was superphosphate from bone ash; tables show the effects of different quantities of phosphoric acid, but the net result is stated to be 1 part of soluble phosphoric acid in superphosphate equals 2·1 parts of finely ground slag and 5·6 of coarsely ground.

Three series of experiments were again made with other crops and manures, of which a summary gives the following comparative results. Counting the increase yielded by superphosphate of 18·74 per cent. soluble phosphoric acid as 100, the other manures show—Superphosphate, 100; Peruvian guano, 30; bone meal, 10; ground coprolites, 9; three samples of Thomas slag of different degrees of fineness, 61, 58, 13.

The fineness of the ground slag has a very great effect on the yield, and the author recommends certain precautions to the buyers to secure fineness. It has been said that the presence of iron would prove injurious to the crops, but the author did not find such to be the case.

The slag is recommended to be used on moorlands or humous soils, where it produces better results than on purely mineral soils; for meadows, potash salts should be added, and on mineral soils double the usual quantity of phosphoric acid. Sulphate of ammonia should not be added to the slag, as it is decomposed with loss of ammonia; where peat mould is available, a small quantity is recommended to be mixed with it. J. F.

Analytical Chemistry.

Indirect Determination of Chlorine, Bromine, and Iodine by the Electrolysis of their Silver Salts, &c. By J. E. Whitfield (*Amer. Chem. J.*, 8, 421—426).—The indirect estimation of any two of the halogens may be effected satisfactorily by precipitating both

together as silver salts, collecting on an asbestos filter, washing, drying at 150°, weighing, dissolving the residue in potassium cyanide, and either electrolysing the solution to determine the silver or precipitating the silver as iodide; again collecting on asbestos, washing, drying, and weighing. In a mixture of all three halogens, the iodine is first separated by known methods, and the chlorine and bromine indirectly estimated as described. H. B.

Estimation of Sulphur in Soluble Slags. By E. D. Campbell (*Chem. News*, **55**, 74).—The slag is decomposed by means of hydrochloric acid with the addition of bromine, the mixture is gradually heated, and then boiled. The solution is filtered and the oxidised sulphur precipitated with barium chloride. D. A. L.

Absorption of Nitric Oxide by Sulphuric Acid. By F. Nettlefold (*Chem. News*, **55**, 28—29).—The author treated different samples of guncotton and nitre with sulphuric acid and measured the nitric oxide evolved; on now adding more sulphuric acid and measuring again, absorption of nitric oxide was observed in all cases, the quantity varying with the substance employed, but never exceeding a few hundredths per cent. of the total nitric oxide. With pure nitric oxide, no such absorption was observed. The acid employed had a sp. gr. of 1·842. D. A. L.

Detection of Phosphorus by Mitscherlich's Method. By — Mankiewicz (*Arch. Pharm.* [3], **25**, 32).—0·001 gram of phosphorus in 200 grams of 3 per cent. carbolic acid water does not give the characteristic phosphorescence, and so would be overlooked; with 0·002 gram even, the test fails; but with 0·005 gram it succeeds. J. T.

Simplified Method for the Estimation of Phosphoric Acid from the Weight of the Molybdenum Precipitate. By E. Thilo (*Chem. Zeit.*, **11**, 193—195), A. Isbert (*ibid.*, 223), and Laible (*ibid.*, 286).—The reducing action of the filter-paper is adduced as a constant but variable source of error in estimating phosphoric acid by weighing the dried molybdenum precipitate, and as the mechanical removal of the precipitate from the filter cannot be effected without some loss, the author proposes and fully describes a method of dissolving the molybdenum precipitate in standardised ammonia, titrating any excess with standard acid, and calculating the percentage of phosphoric acid from the amount of ammonia required to dissolve the precipitate. As silica does not interfere with the working of the method, its previous removal is superfluous. For the precipitation of phosphoric acid, a relatively small excess of molybdate is sufficient.

Isbert has made experiments in the above direction, both with ammonia and soda, and with numerous indicators for the titration, but could not get concordant results. He points out that the molybdic precipitate always contains more or less molybdic acid, which of course affects the results; moreover the end reaction with the indicators is either indistinct or not visible. He suggests a method based on the determination of the ammonia in the precipitate.

Laible shows that the results obtained from the determinations of both ammonia and nitrogen in both the molybdenum precipitate and in ammonium magnesium phosphate, cannot be used as a basis for the calculation of the percentage of phosphoric acid, inasmuch as the percentage of ammonia in the molybdenum precipitate is not constant. In the case of the ammonium magnesium phosphate, when the precipitate is washed with water owing to its solubility the results are low; and on the other hand, when it is washed with ammoniacal water and dried, the results are also low, owing presumably to loss of ammonia while drying. D. A. L.

Determination of Phosphorus in Iron and Steel. By L. Schneider (*Chem. Centr.*, 1887, 45).—If the solution of iron in nitric acid is not evaporated to dryness, and the dry mass strongly heated, the molybenum method always gives too low a percentage of phosphorus. The cause of this error is that the phosphorus is not completely oxidised to phosphoric acid by simple solution in nitric acid; a portion goes into solution as phosphorous acid, and so escapes precipitation with ammonium molybdate. It is necessary, therefore, to evaporate and heat the iron nitrate in order to complete the oxidation. G. H. M.

Determination of Phosphorus in Basic Slag. By C. Brunnemann (*Chem. Zeit.*, **11**, 19—20).—The author at the present time carries out his process as follows:—10 grams of the slag are digested with 50 c.c. of water; 100 c.c. of hydrochloric acid, 50 c.c. of nitric acid, and 10 c.c. of strong sulphuric acid are added, and the whole is boiled for half to three-quarters of an hour. The hot liquid is poured into 400 c.c. of hot water in a litre flask; the calcium sulphate is dissolved by further diluting and shaking; the cooled mixture is made up to a litre, and the silica, sand, and carbon are allowed to subside. Of the clear liquid, 50 c.c. is evaporated until the hydrochloric and nitric acids are expelled; the sulphuric acid is neutralised by careful addition of ammonia; the whole is evaporated to dryness and heated to 110° to render the silica insoluble. The mass is rubbed up with 10 c.c. of strong nitric acid; 50 c.c. of hot water are added; the silica is filtered off, and the phosphoric acid is precipitated by molybdate as usual. By this method, the phosphorus of the iron phosphide is reported as phosphoric acid, which, in the author's opinion, is justified by the rapidity with which it oxidises in the soil. M. J. S.

Determination of Phosphoric Acid in Basic Slag. By G. Loges (*Chem. Centr.*, 1887, 229).—The author recommends that the slag should be attacked with concentrated sulphuric acid, avoiding oxidising agents. He considers that the phosphorus of the iron phosphide should not be converted into and reported as phosphoric acid, since, although it undergoes oxidation in the soil, its value as a manure is not equal to that of the ready formed phosphate. M. J. S.

Estimation of Silicon in Iron. By G. H. Stbick (*Dingl. polyt. J.*, **262**, 384).—2 grams of iron is dissolved in dilute sulphuric acid, and the solution evaporated to expel all water. The iron sulphate is then

dissolved in water, and the silicic acid filtered off and determined in the ordinary way. This analysis is completed in one and a half hours, whilst the error does not exceed 0·1 per cent. D. B.

Speedy Volumetric Determination of Carbonic Anhydride. By W. Marcet (*Proc. Roy. Soc.*, **41**, 181—195). — The method, described at length, is based on the absorption of carbonic anhydride in a closed receiver by potassium hydroxide, and the accurate measurement of the volume of dry atmospheric air required to re-establish the atmospheric pressure after complete absorption. The volume of air will correspond with the volume of the carbonic anhydride, and the weight of the latter is deduced by the ordinary method of calculation. The process consists in passing the air to be analysed from one of two small gasometers through an absorption apparatus into the other, the amount of absorption being recorded by a pressure-gauge. Air is then added from a small receiver enclosed over mercury until the atmospheric pressure in the whole apparatus is restored, and the volume of air thus added is read off.

Certain mechanical difficulties were at first experienced, and the methods by which they were successfully overcome are described in full. Comparative analyses made by this method and by Pettenkofer's are given; the latter, as a rule, gives slightly lower results than the former, the average difference being about 0·4 per cent.

V. H. V.

Detection of Normal Carbonate in Hydrogèn Carbonates of the Alkali Metals. By E. Kuhlmann (*Arch. Pharm.* [3], **25**, 72—73).—A concentrated solution of pure hydrogen sodium carbonate to which a fragment of rosolic acid has been added remains perfectly colourless, even after standing a quarter of an hour. If 1—4 per cent. of normal carbonate is present a rose tint very shortly appears. If over 4 per cent. is present, the colour rapidly becomes purple. With potassium carbonate, the reaction is more sensitive. Previous writers have noted the sensitiveness of phenolphthaleïn as a test, in fact, it is too sensitive for commercial purposes in this application.

J. T.

Separation of Sodium and Potassium from Lithium, Magnesium, and Calcium by the Action of Amyl Alcohol on the Chlorides. By F. A. Gooch (*Chem. News*, **55**, 18—19, 29—30, 40—41, 56—57, 78—79).—After criticising the methods previously adopted for the estimation of lithium in the presence of potassium and sodium, and exposing their weak points, the author proceeds to compare the relative solubilities of lithium, potassium, and sodium chlorides in amyl alcohol, and he finds that 1 part of lithium chloride requires 15 parts of this solvent, 1 of potassium chloride 24,000 parts, and one of sodium chloride 30,000; and when used to wash the solid chlorides the quantity of potassium or sodium chloride dissolved is quite insignificant. It is upon this basis that the following accurate method of separating and estimating lithium in the presence of potassium and sodium is founded.

Amyl alcohol is added to the concentrated solution of the chlorides, the mixture is heated gently at first until the water is driven off, it is

then raised to boiling temperature and boiled; potassium and sodium chlorides are precipitated, lithium chloride passes into solution; the liquid is now allowed to cool, a few drops of hydrochloric acid added to convert any lithium hydroxide into chloride, then it is boiled again to drive off water.

If great accuracy is required, and the quantity of lithium exceeds 10—20 mgrms., the liquid is decanted off, the residual chlorides washed with amyl alcohol, then redissolved in water and re-treated. The combined extracts and washings are evaporated to dryness, treated with sulphuric acid, ignited, fused, and weighed. For details of the precautions required, the original paper should be consulted. Magnesium and calcium chlorides are also soluble in amyl alcohol, they may therefore be separated from sodium and potassium chlorides in the manner described above: in the case of calcium chloride, a second treatment is always necessary. Preliminary experiments indicate the probable extention of the method to nitrates. D. A. L.

Separation of Metals by Oxalic Acid. By C. Luckow (*Chem. Zeit.*, **11**, 5—6). (See Abstr., 1886, 922.)—Of the metals of group 6, oxalic acid precipitates tin and antimony when occurring as stannous and antimonious salts, but not when in the state of stannic and antimonic compounds. Arsenic is not precipitated, and solutions of arsenious chloride mixed with oxalic acid may be evaporated without loss of more than traces of the metal. From a solution containing the three metals and oxalic acid, ammonia precipitates the tin only. All the metals of group 5 are precipitated by oxalic acid. The oxalates of lead, bismuth, silver, copper, and mercury are almost absolutely insoluble; that of cadmium is very sparingly soluble. All are the denser if thrown down by boiling oxalic acid. Of the fourth group, oxalic acid precipitates nickel, cobalt, manganous, ferrous, and uranous oxides (but not the corresponding higher oxides), also zinc from neutral or moderately acid solutions. They require a longer time for complete separation than those of the fifth group; addition of ammonium chloride or nitrate favours their precipitation, but the best way, especially with zinc, is to evaporate to dryness. Dilute sulphuric and nitric acids do not greatly increase the solubility of the precipitates; hydrochloric and strong oxalic acid have a much greater solvent action. Many of the precipitates dissolve in alkaline oxalates. The exceptions are the strontium, barium, calcium, silver, lead, and mercuric salts. The barium, magnesium, and mercuric oxalates dissolve in ammonium chloride. M. J. S.

Analysis of Copper. By W. Stahl (*Dingl. polyt. J.*, **262**, 277—278).—In estimating copper by electrolysis, it is recommended to remove all traces of lead and silver, as the latter is deposited at the cathode together with the copper whilst the lead is retained by the anode, thus causing too much resistance to the passage of the current. The addition of nitric acid to the sulphated electrolyte is said to exert a beneficial effect on the passage of the current, and prevent the volatilisation of arsenic and antimony at the cathode. In most cases, the electrolytic action may be continued until the colour of the

electrolyte has been entirely removed without the risk of depositing antimony or arsenic. Bismuth, if present, is separated with the copper and is removed by dissolving the total deposit in dilute nitric acid, treating the solution with hydrochloric acid, evaporating to dryness, and precipitating the bismuth as oxychloride. This treatment should be repeated for the purpose of removing basic cupric chloride which is carried down with the oxychloride. The precipitate is then dissolved in dilute nitric acid, the solution neutralised with ammonia, precipitated with ammonium carbonate, ignited, and weighed as bismuthic oxide. D. B.

Employment of Nitroso-β-naphthol in Quantitative Analysis. By G. v. Knorre (*Ber.*, **20**, 283—290; compare Ilinski and v. Knorre, Abstr., 1885, 840; 1886, 100).—Copper can be separated from lead, cadmium, magnesium, manganese, mercury, zinc, and other metals, by precipitation as *copper nitroso-β-naphthol*, $Cu(O{\cdot}C_{10}H_6{\cdot}NO)_2$. This is obtained as a coffee-brown precipitate of metallic lustre. The separation is effected by neutralising with ammonia the solution, which must contain the metals as sulphates or chlorides, acidifying with a few drops of hydrochloric acid, heating nearly to boiling, and adding excess of nitroso-β-naphthol dissolved in 50 per cent. acetic acid; after remaining for some hours in the cold, the precipitate is collected, dried, ignited, and weighed as cupric oxide. The separation of iron from chromium, manganese, nickel, zinc, &c., can be effected by the method previously given for its separation from aluminium (*loc. cit.*). Full details of the methods and of the results of test analyses are given in the original. A. J. G.

Detection of Alum in Flour. By J. Herz (*Dingl. polyt. J.*, **262**, 96).—A glass cylinder is filled from one-fourth to one-third full with the flour to be examined and the flour is moistened with water. It is then treated with a few c.c. of alcohol and two drops of a freshly-prepared solution of logwood (5 grams logwood in 100 c.c. of alcohol). After agitating the mixture, the cylinder is filled up with a saturated solution of sodium chloride. The depth of colour of the salt solution is then compared with that obtained by treating pure flour and flour containing 0·01 per cent., 0·05 per cent., and 0·1 per cent. of alum in a similar manner. The colour is permanent for days, being blue in presence of 0·05—0·1 per cent. of alum, and violet-red with 0·01 per cent. D. B.

Detection of Free Sulphuric Acid and of Aluminium Hydroxide in Aluminium Sulphate. By K. J. Bayer (*Chem. Zeit.*, **11**, 53).—Referring to Hager's note (this vol., p. 182), the author remarks that free sulphuric acid is detected more readily and with greater certainty by the use of tropæolin as previously described (Abstr., 1886, 281; 651). If aluminium sulphate contains aluminium hydroxide which passes into solution as basic salt, it can be quantitatively determined by titration with normal sulphuric acid, using tropæolin as indicator. The turbidity noticed by Hager (*loc. cit.*) when dissolving aluminium sulphate in 2 parts of water, is due either

to silicic hydroxide or to the basic sulphate, $3Al_2O_3,2SO_3 + 9H_2O$ (this vol., p. 448). D. A. L.

Volumetric Estimation of Manganese. By C. Meinecke (*Chem. Zeit.*, **11**, 137—138).—The author, in his earlier determinations of manganese by the chlorate precipitation method (compare Hampe. Abstr., 1885, 101), generally found that when iron was present, some of the manganese passed into the filtrate. This is now traced to the use of warm water for diluting. It appears that in presence of iron, although not otherwise, warm dilute nitric acid dissolves some of the precipitated manganese peroxide. When, after precipitation, the liquid was cooled and diluted with cold water, the whole of the manganese was found in the precipitate. M. J. S.

Electro-dissolution and its Use in Analysis. By H. N. Warren (*Chem. News*, **55**, 62).—By placing iron boride at the positive pole with a platinum plate as the negative pole of a powerful battery, and using dilute sulphuric acid as a solvent, in 12 hours all the iron had dissolved, whilst the boron and other impurities were precipitated. A similar result was obtained with ferrous sulphide, whereas with silicon-iron and phosphide of iron, zinc, &c., the silicon and phosphorus respectively were only partially precipitated. In hydrochloric acid, copper may be separated from arsenic, iron, zinc, &c., by electro-dissolution; and in ammonia, copper silver, zinc arsenic, and other alloys, may be resolved into their constituent metals. Electro-dissolution has also been applied to the preparation of unstable compounds, such as potassium ferrate, &c. D. A. L.

Detection of Adulteration in Metallic Nickel and other Metals, by the Magnet. By T. T. P. B. Warren (*Chem. News*, **55**, 37).—In a mixed sample of nickel cubes, some were found to be non-magnetic, and the sample was easily separated into two lots by means of a magnet. The non-magnetic cubes were a trifle whiter and had not the striated structure noticeable in the magnetic cubes, but there was no marked difference. On analysis, the following results were obtained:—

	Ni.	Cu.	C.	SiO_2.	Fe.	As.	Sn.
Magnetic.....	96·67	0·08	0·07	0·41	2·46	0·12	0·75
Non-magnetic...	63·69	33·78	0·37	0·16	0·84	0·87	0·46

Other experiments show that the magnetic properties of both nickel and cobalt are affected by alloying with para-magnetic metals. Moreover, manganese and other metals are met with in commerce without magnetic properties.

When nickel apparatus is heated over a Bunsen flame, a black deposit forms, consisting mainly of graphitoidal carbon with traces of nickel, iron, and silica; therefore, the naked flame should not impinge on such apparatus. Other modes of heating are suggested. D. A. L.

Detection and Determination of Traces of Chromium. By E. Donath and R. Jeller (*Chem. Centr.*, 1887, 151).—If a solution

containing a chromic salt is boiled with sodium carbonate and potassium permanganate, the chromium is oxidised to chromic acid. On re-boiling with addition of alcohol, the permanganate is reduced and the manganese precipitated together with any iron, aluminium, manganese, or alkaline earths previously present. The chromate may be recognised by its colour or by adding sulphuric acid, potassium iodide, and starch. This reagent is more sensitive than hydrogen peroxide. For determination, the solution is re-boiled with alcohol after acidifying, and the chromium is precipitated by ammonium sulphide as usual.

M. J. S.

Analysis of Chrome Iron Ore. By W. Venator and E. Etienne (*Chem. Zeit.*, **11**, 53).—The mineral is decomposed by fusion with caustic soda, and when cold is dissolved in hot water, treated with hydrochloric acid, evaporated to dryness, and dried for some time at 120°; the silica is then separated in the usual manner. Ammonium chloride and ammonia are added to the filtrate, and calcium and magnesium are determined in the solution; whilst the precipitate of aluminium, iron, and chromium hydroxides is weighed and fused with soda, the fused mass is boiled out with water and mixed with excess of ammonium carbonate. The solution is evaporated to dryness and treated with water, the sodium chromate then passes into solution, leaving the iron and aluminium oxides behind. To estimate the chromium, the chromate is reduced by means of sulphurous anhydride, the excess of the latter boiled off, and the chromium precipitated by ammonia in a platinum vessel. Concordant results have been obtained.

D. A. L.

Determination of Organic Matter in Air. By T. Carnelley and W. Mackie (*Proc. Roy. Soc.*, **41**, 238—247).—Of the methods proposed for the estimation of organic matter in air, one consists in causing the air to bubble slowly through a dilute solution of potassium permanganate until the latter has become quite or nearly decolorised, any undecomposed permanganate being subsequently estimated by oxalic acid; the other consists in passing the air through distilled water in which the free and albuminoïd ammonia are subsequently determined by Wanklyn and Chapman's process. Both these methods, however, are tedious, and uncertain as regards the decomposition of the permanganate in the first, or the absorption of the organic matter by the water in the second. For the process described below, the authors claim rapidity and simplicity, a greater probability of exactness, and a more general applicability. The method proposed consists in a colorimetric estimation of the diminution of colour of a potassium permanganate of known strength, that is to say, the fractional bleaching of the solution effected by a given volume of air. The tint of the permanganate after passage of the air is compared with that of a standard solution of known tint. The method of procedure and the necessary precautions are described in full. Although the method gives concordant results, yet it is fully allowed that the organic matter is not directly estimated by it, that other gases likely to be present in air, such as hydrogen sulphide, nitrous and sulphurous acids, equally decolorise the permanganate, and that as the organic

matter in air is of various kinds, the permanganate is selective in its action. Determinations are given of the organic matter and carbonic anhydride in samples of air under various atmospheric conditions, by which it is shown that these vary in a somewhat similar manner, the results being lower immediately after or during rain or snow, and higher during fog and mist. The organic matter in air exhibits a wider range of variation than the carbonic anhydride. The effects produced by the combustion of coal-gas and paraffin oil as also by respiration are likewise investigated. As regards the last, although the carbonic anhydride and organic matter vary alike to some degree, yet the determination of the former affords no adequate index of the proportion of the latter. After a time, the air is found to contain less organic matter than it did previously; this is owing to the organic matter present being partly gaseous and partly solid; the solid slowly settles down, whilst the gaseous part more readily undergoes oxidation. V. H. V.

Colorimetric Determination of Nitrites in Water. By L. Zambelli (*Chem. Centr.*, 1887, 45).—Two methods for this purpose are proposed, to the first of which the author gives the preference. This consists in adding a solution of sulphanilic acid in dilute sulphuric acid to 200 c.c. of the water under examination, after allowing this to remain for 10 minutes, a little aqueous solution of α-naphthol is added, and the mixture made alkaline with ammonia. If nitrites are present the liquid is coloured rose to deep-red. The reaction is given by water containing 1 part nitrous acid in 25,000,000. In the second method, the α-naphthol is replaced by phenol. Nitrites when present in even smaller quantities than 1 in 40,000,000, give with this reagent a yellow coloration, which remains unchanged for a considerable time. This reaction can be applied to the comparative colorimetric estimation of nitrites in water. G. H. M.

Determination of Organic Matter in Natural Water. By A. Köbrich (*Chem. Zeit.*, **11**, 4).—The author, observing that determinations of the amount of organic matter in waters are not comparable when made by different processes, proposes that the amount should always be stated as equivalent to so much oxalic acid, and that it should be determined by ascertaining the amount of potassium permanganate reduced by it under the following conditions. A solution containing 0·5 gram of permanganate in 1 litre is mixed with 150 grams of pure concentrated sulphuric acid, and maintained at 90° for three hours. Of the solution thus prepared, 50 c.c. are added to 100 c.c. of the water, then 15 c.c. of concentrated sulphuric acid, the mixture is heated for three hours at 90° and the amount of permanganate reduced is ascertained by titration with oxalic acid. The large quantity of acid, added in the concentrated state, the high temperature, and the prolonged heating, are the essential features of the process. Chlorides must first be removed by adding silver nitrate and filtering. Nitrites are to be oxidised by adding the permanganate to the cold, feebly acidified water, until the colour is permanent for five minutes. M. J. S.

Detection of Dextrose. By C. Agostini (*Chem. Centr.*, 1887, 99).—Five drops of the liquid to be tested are taken, and five drops of a solution of gold chloride (1 : 1000), and two drops of potassium hydroxide solution (1 : 20) added, and the whole heated. If dextrose is present, the liquid shows, on cooling, a beautiful violet coloration, more or less intense, depending on the amount of dextrose present. 1 part of dextrose in 10,000 can be detected by this reaction. With urine containing sugar, a wine-red coloration is given. The author has examined a large number of normal and pathological urines, and finds that none of the normal or abnormal constituents of urine, with the exception of albumin, interferes with this reaction. If albumin is present, it must be removed by boiling and filtration. G. H. M.

Colour Reactions of Beet-sugar. By A. Ihl (*Chem. Zeit.*, **11**, 2—3; see Abstr., 1885, 694).—The colour reactions which occur when sugar is heated with a phenol and an acid are due to the presence of the humous substances resulting from the action of acids on sugar (Abstr., 1885, 745). Caramel gives similar reactions. The shades of colour vary somewhat according to the method of operating. With hydrochloric acid, it is generally necessary to warm, but strong sulphuric acid usually produces sufficient heat for the reaction. A mixture of sulphuric acid and alcohol may be used with advantage. Resorcinol, pyrogallol, thymol, cresol, and guaiacol give red shades; α-naphthol, violet; orcinol (in presence of alcohol) a deep yellow solution, from which a green precipitate separates on adding water. Molisch obtained the naphthol reaction with a solution containing only 0·00001 per cent. of sugar. (See next Abstract.) M. J. S.

Behaviour of Sugar towards Acids and Phenol. By B. Tollens (*Chem. Zeit.*, **11**, 77).—In reference to Molisch's sugar reaction (Abstr., 1886, 923), it has been suggested that the coloration is due to a combination of the phenols with the humous substances produced from the sugar (preceding Abstract). The author's experiments prove this suggestion to be quite fallacious, inasmuch as the phenols give brownish-black resinoid substances with the humous matter from sugar. In fact this reaction may be used with advantage to remove such substances from sugar solutions; as, for instance, in the preparation of lævulinic acid from cane-sugar the humous substances may be completely separated by treatment with phenol.

D. A. L.

Colour Reactions of Starch and Gums. By A. Ihl (*Chem. Zeit.*, **11**, 19).—All the carbohydrates give somewhat similar reactions with the phenols in presence of sulphuric or hydrochloric acid. Starch, however, requires a higher temperature than sugar. Starch moistened with alcoholic solution of α-naphthol and a few drops of warm concentrated sulphuric acid, acquires a deep violet-red colour. Thymol, cresol, guaiacol, and catechol give cinnabar-red, orcinol and resorcinol a yellowish-red, phloroglucol a yellowish-brown.

With the gums, similar appearances are produced. Arabin boiled with an alcoholic solution of phloroglucol and strong hydrochloric acid affords a characteristic cherry-red dye. M. J. S.

Determination of Hippuric Acid in Urine. By O. Völcker (*Chem. Centr.*, 1887, 124—125).—200—300 c.c. of urine are evaporated down to one-third in a glass basin of 100 c.c. capacity, about 4 grams of sodium dihydrogen phosphate added, and the evaporation continued until the liquid is syrupy; highly-burnt calcium sulphate is then added, and the whole heated until the mass becomes pulverulent. The residue is collected and extracted in a small Soxhlet's apparatus with rectified light petroleum; after four to six hours the flask is changed, and the extraction continued with dry ether free from alcohol for six to ten hours. After a time, crystals of hippuric acid separate from the ethereal solution. The ether is distilled off, and the dark-coloured residue dissolved in hot water, decolorised with animal charcoal, the solution filtered, and the charcoal washed with hot water. The solution is evaporated to 1 to 2 c.c. on a water-bath at 50—60°, and allowed to crystallise. The crystals are collected on a tared filter-paper dried at 110°, the dish washed out with the filtrate, and the latter collected in a graduated cylinder. The filter is washed with a few drops of water, then with a little ether, dried at 100°, and weighed. 0·0015 gram for every c.c. of the filtrate is added to the weight, in order to correct for the hippuric acid in solution. The results obtained by this method are very good. G. H. M.

Characteristics of Olive Oil. By A. Levallois (*Compt. rend.*, **104**, 371—373).—The author has examined a large number of genuine samples of olive oil from the olive yards of the south-east of France.

The colour of the oil was determined by means of a Duboscq colorimeter. The colour at the commencement of a crop is 70 times as intense as at the end. The sp. gr. at 15° varies from 0·9167 to 0·9177. and the differences observed with different species are only very slight. The sp. gr. of olive oil at 24° is 0·911, whilst that of other oils at the same temperature is as follows:—

Sesame.....	0·917	Colza	0·910
Cotton-seed.....	0·9165	Camelina	0·920
Earth-nut	0·912	Linseed	0·928
Poppy	0·9205		

The sp. gr. of colza and earth-nut oil are somewhat near that of olive, but their other properties make it easy to distinguish between them.

Cailletet's reagent (nitric acid saturated with nitrogen oxides) usually gives a green coloration, which, however, is not always pure, but is sometimes mixed with yellow.

Audoynaud's reaction (addition of nitrosulphuric acid and ether to a mixture of the oil with potassium dichromate) usually gives a green coloration, which in some cases is mixed with yellow.

The determination of the non-saturated fatty acids by treating the non-saponified oil with bromine or iodine gave no concordant results. The following method is satisfactory:—5 grams of the oil are weighed into a test-tube about 15 cm. long and 15 mm. diameter, mixed with

10 c.c. of a 20 per cent. solution of potassium hydroxide in alcohol of 93°, and agitated, when the oil dissolves. The liquid is then heated on a water-bath to a temperature sufficient to produce gentle ebullition, and after about 15 minutes saponification is complete. The volume of the liquid is then made up to 50 c.c. by adding alcohol, and 5 c.c. of the solution is placed in a tube provided with a glass stopper, acidified with hydrochloric acid, and then mixed with a concentrated aqueous solution of bromine from a burette, with vigorous agitation, until the liquid acquires a persistent pale-yellow tint. About 0·1 c.c. of solution is required to produce the end reaction, and this should be subtracted from the total volume added. The bromine is standardised by means of a decinormal solution of arsenious acid, mixed with hydrochloric acid. Different samples of oil from the same species of olive absorbed from 0·512 to 0·522 gram of bromine per gram of oil. The absorption by oil from different species of olive varied from 0·500 to 0·544, the last result being obtained with oil from Blanquetier which also has an exceptionally high sp. gr. The amount of bromine absorbed by 1 gram of other oils is as follows:—

Cotton-seed	0·645	Colza	0·640
Sesame	0·695	Camelina	0·817
Earth-nut	0·530	Linseed	1·000
Poppy	0·835		

The alcoholic solution of soap from oil of earth-nut becomes solid as soon as the temperature falls to 15°, but the corresponding solution of olive oil soap remains liquid.

The most constant characteristic of olive oil is its sp. gr., but the determination of the bromine absorbed is also very useful.

C. H. B.

Properties of Olive, Sesame, and Cotton Oils. By T. Leone and A. Longi (*Gazzetta*, **16**, 393—398).—The authors, with a view to the recognition of the presence of sesame and cotton oils in cases of sophistication of olive oil, have examined the physical and chemical properties of these oils, such as the proportion of solid acids obtained on saponification, the quantity of alkali required to complete this process, the specific gravities at 100° of the oils and the resultant acids, the points of fusion and solidification of the acids, and the indices of refraction of the oils. As a result of their examination, it follows that the quantities of solid acids and of alkali required for saponification are appreciably equal for all three oils, but the sp. gr. of olive oil at 100° is less than that of sesame and cotton oils by about 0·005, the index of refraction of the former is also somewhat less than those of the latter. But the most marked difference is observed in the points of fusion and solidification of the resultant acids, for those from olive oil melt at 24—27°, and begin to solidify at 17·5°, whilst those from cotton and sesame oils melt at 36—40°, and solidify at 34—30° and 34—32° respectively.

V. H. V.

General and Physical Chemistry.

Spark Spectra from Coils of Low Tension. By E. Demarçay (*Compt. rend.*, **104**, 678—679).—The author modifies his previous statement respecting the identity between the spectra obtained by coils of low tension and those obtained with the electric arc.

The spectra of potassium, sodium, thallium, and aluminium seem identical under both conditions; those of barium, strontium, and calcium seem identical except as regards the intensities of the lines. The spectra of tin, lead, and mercury are, however, very different, and are not similar to those described by Hartley and Adeney. So far as the visible portion of the spectrum is concerned, they seem to differ but slightly from those described by Boisbaudran.

The lines of fluorine are obtained by allowing the sparks to fall on concentrated hydrofluoric acid, and the spectrum is similar to that described by Salet. Oxygen lines are obtained in the same way from water, pure dilute acids, and fuming nitric acid. The line at 6160 which appears under these conditions seems to be due to oxygen, and is probably identical with the line described as 6171 by other observers. There are also violet and blue lines which seem to be due to oxygen. C. H. B.

Variations in the Absorption Spectrum of Didymium. By H. Becquerel (*Compt. rend.*, **104**, 777—780).—When the absorption spectra of different natural or artificial crystals which contain didymium in various states of combination are compared, it is found that a great number of characteristic bands occur in these spectra, but their wave-lengths vary in different cases. The variations do not affect the whole spectrum. One set of bands will be displaced in a certain direction, whilst another set remains in its original position. In some cases, certain bands are wanting. Differences of the same order are observed when the crystals are dissolved in water. In the solutions, the different principal absorption spectra of the crystals are superposed, and the bands which disappear in certain directions in the crystals will be more or less diminished in intensity in the solution, and other bands may lose their distinctness by reason of the juxtaposition of several bands belonging to different principal spectra. Apart from these modifications, it is found that the solutions show all the principal bands observed in the corresponding solids, some retaining their positions, whilst some are displaced in one direction, others in the other direction.

No variations of this irregular character are observed in the case of uranium; any cause which affects one set of bands affects the others in the same direction.

The phenomena observed in the case of didymium can be readily explained if it is assumed that each of the variable bands is due to a distinct substance. A table which is given shows the nature of

the variations for certain cases. The majority of the variable bands can be attributed to different substances; for example, the three bands of praseodidymium, 4819, 4690, 4450, and the group at 4755, and the bands of neodidymium, 5710, 5239, 5214, 5205, 5115, 4270. The spectra of the solutions of double nitrates are all identical, but the spectra of the crystals show distinct differences, a fact which would indicate that the double compound is decomposed when dissolved. The bands which have been enumerated are those which have a particular direction of absorption in the crystals, and several of them have been separated by chemical processes.

The bands show both a chemical and crystallographic individuality, but it is not at present possible to decide whether they are due to distinct simple substances. The substances which produce the bands have certain of the properties which characterise simple substances, and it may be that some of the substances to which the bands are due are either very stable combinations of two substances or polymeric modifications of the same substance. C. H. B.

Red Fluorescence of Alumina. By L. de Boisbaudran (*Compt. rend.*, **104**, 478—482, 554—556).—Alumina was prepared from aluminium chloride by decomposing it with water, evaporating the solution to dryness, and heating to a temperature sufficiently high to produce the red fluorescence with alumina from alum. The fluorescence of the alumina thus obtained was not red, but blue to greenish-blue, and its spectrum gave neither a line nor a band. The addition of 0·1 per cent. of chromic oxide, however, produced a brilliant red fluorescence far brighter than that obtained from pure alumina under any conditions, and the bands in the spectrum are well defined. With 0·01 per cent. of chromic oxide, the fluorescence is rose-red, and the band and line in the spectrum are very distinct. 0·005 per cent. of chromic oxide produces a mixture of the greenish-blue and rose-red fluorescence, which is generally of a rosy-white tint.

Moderately calcined alumina mixed with about 1 per cent. of bismuth oxide shows at most a very feeble greenish fluorescence.

A strongly calcined mixture of bismuth oxide and alumina from the sulphate shows a reddish-lilac fluorescence. If the alumina has been prepared from alum, the fluorescence is a mixture of the pale-green and dull red fluorescences; if from aluminium chloride, the fluorescence is almost white with a greenish or violet tinge. When the exciting current is weak, the violet tinge only is seen. With a much smaller proportion of bismuth oxide (0·065 per cent.), the fluorescence is brighter, and has a greenish-blue tinge. It is distinctly brighter than with 1 per cent. of the oxide, and much brighter than with pure alumina.

The curious fluorescence, lilac in the cold but blue on heating, which is obtained with alumina prepared from the sulphate mixed with bismuth oxide, seems to be due to the simultaneous presence of bismuth and some other substance, but the latter is not potassium.

The red line seen in the spectrum of the fluorescence of alumina from alum, &c., disappears when the tube is moderately heated in a

vacuum, and at the same time the fluorescence becomes orange. The broad red band in the spectrum at first becomes more intense, but if the tube is more strongly heated the band disappears.

Alumina mixed with a small proportion of ferric oxide and very strongly heated gives no red fluorescence. Alumina from alum containing 1 per cent. of cupric oxide and moderately calcined, shows a somewhat bright bluish-green fluorescence. After strongly heating, the red fluorescence is obtained.

Alumina from alum gives the most intense fluorescence when it is precipitated by ammonia, and at first gradually and then very strongly heated. Alumina from alum which has been very strongly heated, and containing 0·001 per cent. of manganese oxide, but free from potassium oxide, gives a pale-rose fluorescence with the red band in the spectrum well marked. Here and there the fluorescence is greenish.

The red obtained from pure alumina in the phosphoroscope is much feebler than that given by less pure varieties of the oxide, especially if the latter contain a small quantity of chromium. There is no spectrum evidence to show whether the two fluorescences are or are not identical.

Pure alumina prepared from redistilled aluminium chloride by precipitation with ammonia and calcination at a high temperature, gives a feeble red phosphorescence in the phosphoroscope. If the aluminium chloride is decomposed by a small quantity of water, the solution simply evaporated to dryness, and the residue strongly heated, the alumina thus obtained gives a very feeble greenish-white phosphorescence in the phosphoroscope. It would seem that the red phosphorescence observed in the first case is due to impurities introduced either in the form of dust or in the distilled water used for washing.

These results tend to support the author's view that small quantities of chromium are the determining cause of the red fluorescence.

C. H. B.

Causes which Determine the Phosphorescence of Calcium Sulphide. By A. Verneuil (*Compt. rend.*, **104**, 501—504).—The shell of *Hypopus vulgaris* (this vol., p. 2) has the composition $CaCO_3$ 98·21, Na_2CO_3 0·99, NaCl 0·06, insoluble matter 0·04, SiO_2 0·02, MgO 0·01, P_2O_5 traces, organic matter and loss 0·67 = 100.

Pure calcium carbonate mixed with double the proportion of sodium carbonate present in the shell and 0·02 per cent. of sodium chloride, and then heated with 30 per cent. of sulphur and 0·02 per cent. of bismuth nitrate, yields a product which phosphoresces in a manner very similar to that of the product obtained when the shell of *Hypopus* is treated in a similar manner.

Pure calcium sulphide gives no phosphorescence; if mixed with a small proportion of the sulphate it shows a feeble white phosphorescence; with sodium carbonate, a greenish-white phosphorescence; with bismuth added in the form of bismuth nitrate, a feeble white phosphorescence; with sodium carbonate and bismuth simultaneously, a blue phosphorescence. Sodium chloride increases the intensity of the phosphorescences produced by sodium carbonate and by bismuth.

From these and former observations (*loc. cit.*), it appears that the

violet phosphorescence of calcium sulphide prepared from the shell of *Hypopus vulgaris* is due to the simultaneous presence of bismuth oxide, sodium carbonate, sodium chloride, and calcium sulphate. An increase in the proportion of sodium carbonate and chloride above that contained in the shell does not increase the brilliancy of the phosphorescence. Traces of silica, &c., probably exert a similar effect, but their amount is so small that their action is negligeable.

The action of these substances is probably due to the fact that they act as fluxes, and it seems not improbable that all substances which are capable of vitrifying the surface of the calcium sulphide without colouring it render it phosphorescent.

Calcium sulphide becomes phosphorescent to a greater or less extent if heated on platinum foil with a small quantity of borax, potassium carbonate, sodium chloride, sodium carbonate, sodium sulphate, sodium silicate, barium chloride, strontium chloride, calcium fluoride, barium fluoride, barium silicofluoride, cryolite, &c. C. H. B.

Phosphorescence of Calcium Sulphide. By E. Becquerel (*Compt. rend.*, **104**, 551—554).—This paper is mainly a summary of the author's previous observations respecting the phosphorescence of calcium sulphide.

Verneuil's pure calcium sulphide is feebly luminous in the phosphoroscope after being exposed to the sun's rays.

The colour of the phosphorescence of sulphides varies with the temperature. This is well seen in the case of strontium sulphide prepared from strontium oxide and sulphur. At −20° the phosphorescence is violet-blue, at +40° pale-blue, at 90° greenish-yellow, at 150° orange, and the reverse changes are observed as the temperature falls. Strontium sulphide at different temperatures reproduces temporarily and successively under the influence of light almost all the colours of the spectrum. Similar effects are obtained permanently by admixture with foreign substances. C. H. B.

Rotatory Power of Compounds formed in Solutions of Tartaric Acid. By D. Gernez (*Compt. rend.*, **104**, 783—785).—Many substances which, like boric acid, have no action on polarised light, have the power of removing the anomalies of the law of dispersion of solutions of malic and tartaric acids, and of increasing the rotatory power of these substances to a considerable extent. Amongst these are amido-compounds, such as formamide, acetamide, urea; acids, such as arsenic, arsenious, molybdic, and antimonic acids; salts, such as alkaline arsenates, molybdates, and tungstates.

The effect is particularly well seen in the case of sodium molybdate, a very soluble salt. When tartaric acid and sodium molybdate exist together in solution in the proportion of equal equivalents, they form a substance which has a rotatory power 37·57 times as great as that of tartaric acid. The compound formed under these conditions will be $Na_2MoO_4,2C_4H_6O_6$. In solutions which contain a lower proportion of sodium molybdate, the rotatory power is proportional to the amount of the inactive substance up to and even beyond half an equivalent.

The addition of sodium molybdate in quantity above that required by the formula given has no appreciable effect. C. H. B.

Galvanic Element. By W. Borchers (*Dingl. polyt. J.*, **263**, 32—34).—The cell containing the exciting agent consists of an ordinary wrought-iron tube, closed at one end and in which a zinc or tin rod is suspended. The iron tube forms the positive pole. The exciting agent is a solution of sodium hydroxide and sodium nitrate, sodium chloride being added to increase the active power of the solution. For technical purposes the ratio of $Na_2O : NaNO_3 : NaCl = 90 : 80 : 300$ may be used. D. B.

Standard Galvanic Cell. By Gouy (*Compt. rend.*, **104**, 781—783).—A convenient standard of electromotive force is furnished by a cell composed of zinc, zinc sulphate, mercuric oxide, and mercury. The bottom of a flask is covered to a depth of 2 to 3 cm. with carefully purified mercury, a platinum wire sealed into the glass and in contact with the mercury forming the positive pole. On the mercury is placed a layer of yellow mercuric oxide, and the flask is filled with a 10 per cent. solution of crystallised zinc sulphate (sp. gr. 1·06), and in this is immersed a rod of pure zinc, which should be amalgamated. In order to render the cell portable, the zinc may be enclosed in a tube with a narrow aperture closed with some porous material. This arrangement will give a cell with a very high resistance. It matters little whether the cells are exposed to air or are hermetically sealed. Some sealed cells which had been filled up for three months were found to give the same results as freshly prepared cells. The electromotive force, which is equal to about 1·39 volts, does not become constant until after some days. This time being necessary for the mercury to acquire a condition of equilibrium. The electromotive force is independent of the concentration of the zinc sulphate solution, provided that its sp. gr. is above 1·02, and it is not affected by replacing or amalgamating the zinc. It varies very slightly with the temperature, the variations being only 0·0001 per degree between 0° and 30°. If the current does not exceed 0·001 ampère, polarisation rapidly disappears when the circuit is broken, and in practice the circuit is only closed just at the time the observation is to be made. Any effect of accidental closing of the circuit may be avoided by making the internal resistance equal to 1000 ohms. The cell can be used with galvanometers as well as with electrometers.

C. H. B.

Galvanic Polarisation produced by Feeble Electromotive Forces. By C. Fromme (*Ann. Phys. Chem.* [2], **29**, 497—544; **30**, 77—95, 320—343, and 503—530).—The author has made a great number of experiments on the polarisation of platinum, gold, and palladium electrodes. The arrangements were such that the polarisation could be measured by means of an electrometer both during the passage of the current and after the circuit had been broken. By comparison with a neutral plate, the polarisation of each electrode could be separately measured, and the rate of its change during the

passage of the current and after breaking circuit, as well as the influence on it of the presence or absence of air in the voltameter, rise of temperature, and so forth, could be studied. In the first three papers, the results obtained respectively with platinum, gold, and palladium, are described; the fourth contains a *résumé* and discussion. From the latter, the following few observations, bearing specially on the occlusion of gases by these metals, are taken.

Water acidified with sulphuric acid appears to be decomposed even by the weakest currents. Of the liberated gases, one portion condenses on the surface of the electrodes; a second portion penetrates or is occluded by the metal; and a third is either scattered or dissolved in the surrounding liquid. The experiments make it highly probable that oxygen is occluded as well as hydrogen. The electromotive force of polarisation depends solely on the surface-condensed gas; that which has penetrated the electrodes has a great influence on the rate at which polarisation increases or diminishes under different conditions.

The polarisation developed in an air-free voltameter by a feeble current (from one Daniell), approaches the battery electromotive force more nearly the less the total resistance of the circuit. Under no conditions does it actually equal the latter; hence there is always a slight residual current flowing through the cell. The insertion of a resistance into the circuit then diminishes both anode and cathode polarisation. If the charging current has been feeble and of short duration, and the voltameter air-free, the rate of loss of H-polarisation reaches its maximum only after a time; but when air is present part of the hydrogen is at once oxidised, and the polarisation sinks rapidly. When the charging current has been strong, presence of air makes but little difference in the loss of O-polarisation; but with a feeble charging current, presence of air acts so as to increase the original O-polarisation, and hence its rate of change when a resistance is inserted. On the other hand, when the charging current has been long continued, both the electrodes and the surrounding liquid become saturated with gas; the occluded gas slowly leaks out when the charging current is diminished by the resistance, and consequently both polarisations fall away slowly.

The polarisation developed by a current is also affected by the previous condition of the electrodes. The important factor in such cases is occlusion. The occlusion of hydrogen by platinum and palladium is well established; that of oxygen is rendered probable by the fact that when a feeble current is passed successively in opposite directions through a voltameter, and the circuit then broken, the plate which was originally the anode shows at first a slight H-polarisation, which soon gives place to O-polarisation. The occlusion of gases by platinum appears to occur for forces between 0·8 and 1·6 of a Daniell.

A curious phenomenon is observed when two electrodes, previously polarised by a Daniell, are placed in circuit. Both then show equal O-polarisation. This is, partly at least, due to the fact that the original O- was stronger than the H-polarisation. With a stronger charging current (one chromic acid element), the electrodes become

more nearly saturated with gas, and on connecting them both show a transient H-polarisation, which is soon changed to O-polarisation.

The polarisation of either electrode increases as its surface is diminished; that is, it is proportional to the density with which the gas is separated.

An investigation of the rate of loss of both H- and O-polarisation, on open circuit, showed that this is never uniform, but reaches maximum and minimum values. Two explanations of this are suggested. One is, that the union of the occluded gases with the metal is not a union in fixed proportions; and hence the dissociation may show maximum and minimum values. Another rests on the following considerations:—The motion of the occluded gases in the substance of an electrode must always take place in the direction of least saturation, and during charging must be from without inwards. The moment the circuit is broken, a rapid escape of gas takes place from the surface; and there will then be at some little depth a layer of metal highly charged with gas, having on each side of it less saturated layers. For some time afterwards, therefore, the motion will take place in two directions. A series of wave-like motions of the gas will then ensue, which accounts for the maxima and minima. The shorter the duration of the charging current, the more rapidly the gas condensation diminishes from without inwards, and the sooner the rate at which polarisation disappears reaches its maximum. A comparison of these rates for the anode and cathode leads the author to the conclusion that the union of platinum with oxygen is of a looser nature than that with hydrogen, and the motion of the former gas within the electrode more free.

Nevertheless, even when the polarising current has been of brief duration, and the cathode not previously O-polarised, the loss of H-polarisation still reaches a maximum after a distinct interval. This points either to the normal presence of oxygen in the platinum (possibly absorbed during the preliminary heating to redness); or, as Streintz suggests (*Ann. Phys. Chem.* [2], **13**, 644; and **17**, 841), to pure platinum being electronegative towards the same metal containing hydrogen.

The results with gold electrodes are essentially the same as, although somewhat more complex than, those with platinum. They point to the occlusion of gases by this metal for two strengths of battery electromotive force, namely, between 0·2 and 0·7 and above 1·1 Daniell. The presence of air in the voltameter diminishes the force required for occlusion.

The results with palladium are explained by the enormous occlusion of hydrogen, which takes place principally for forces between 0·4 and 1·4 of a Daniell, and by the superficial oxidation of the metal. But even here occlusion of oxygen probably takes place. Only after long passage of a strong current (one chromic acid element) does palladium become completely saturated with hydrogen; and the discharge of this gas when the circuit is broken may then last for weeks.

Warming the voltameter may diminish O-polarisation by scattering the gas; in the same way, it may diminish H-polarisation when this is high, but may increase it by assisting the escape of occluded gas when the polarisation is feeble. Ch. B.

Action of Ethylene Bromide on Alkyl-metallic Oxides: Preparation of Acetylene. By De Forcrand (*Compt. rend.*, **104**, 696—699).—The author's researches on the action of ethylene bromide on alkyl-metallic oxides dissolved in the corresponding alcohols show that the reaction $C_2H_4Br_2$ liquid + 2ROM dissolved in nROH = 2MBr precipitated in n + 2ROH + C_2H_2 gas, develops in the cases of the first five alkyl potassium oxides +15·92; +19·30; +22·44; +32·94; +27·32 Cal. respectively, and in the cases of the first three sodium compounds +1·36; +8·86; +13·66 respectively. The corresponding reaction with the solid compounds develops +41·46; +46·48; +45·94; +50·72, and +44·50 Cal. respectively in the case of the potassium alkyl oxides, and +31·74; +29·18; +33·2; +34·92; +35·02 Cal. respectively in the case of the sodium compounds.

In all these reactions monobromethylene is also produced. The heat of formation of this compound is not known, but the difference between it and y, the heat developed in the above reactions, is greater the greater the value of y. It follows that at the same temperature the proportion of acetylene in the product will be greater, and that of monobromethylene less, the greater the value of y, a conclusion which is confirmed by experiment.

The greatest development of heat is observed in the case of potassium isobutyl oxide, and this compound can be used for the preparation of acetylene. Potassium is dissolved in isobutyl alcohol, the excess of alcohol distilled off in a current of dry hydrogen, and the residue heated at 200° in hydrogen, and after cooling, mixed gradually with ethylene bromide. The reaction takes place at the ordinary temperature, and the gas is purified from isobutyl alcohol and monobromethylene by passing it through absolute alcohol; 500 to 600 c.c. can be obtained from 2 grams of potassium. Potassium ethoxide can also be used, but the gas contains a greater proportion of monobromethylene.

In 1861, Sawitsch (*Compt. rend.*, **52**, 157) obtained acetylene by the action of ethylene bromide on sodium amyl oxide in sealed tubes at 100°; and from potassium ethoxide and propylene dibromide he obtained allylene. C. H. B.

Heat of Formation of Tartar Emetic. By Guntz (*Compt. rend.*, **104**, 699—707).—The heat of formation of potassium hydrogen tartrate was determined by dissolving equivalent quantities of normal potassium tartrate and tartaric acid in dilute hydrochloric acid.

$C_4H_6O_6$ solid + $C_4H_4O_6K_2$ solid = $2C_4H_5O_6K$ solid	develops + 8·0 × 2 Cal.
$C_4H_6O_6$ solid + KHO solid = $C_4H_5O_6K$ solid + H_2O solid	„ +35·1 „

The heat developed by the action of tartaric acid on the normal tartrate is of the same order as that developed by the action of sulphuric acid on the normal sulphate (+7·5 Cal.).

The heat of formation of tartar emetic was determined by dissolving equivalent quantities of potassium hydrogen tartrate and antimony oxide in dilute hydrofluoric acid.

*$C_8H_4O_{10},KO,HO$ solid + SbO_3 solid = HO solid + $C_8H_4O_{10},KO,SbO_3$ solid..... develops −0·85 Cal.

The heat of solution of the anhydrous salt at 12° is −5·1; of the hydrated salt −5·3, whence—

*$C_8H_4O_{10},KO,SbO_3$ solid + HO solid = $C_8H_4O_{10},KO,SbO_3,HO$ solid..... develops −0·5 Cal.

In the process of drying, tartar emetic should not be heated above 100°, since at 110—120° it loses more than one equivalent of water. When heated at 180°, it loses two equivalents of water, as Dumas observed, and forms an anhydride which dissolves in water with development of heat and production of a solution identical with an ordinary solution of tartar emetic.

*$C_8H_2O_8,KO,SbO_3$ solid + H_2O_2 solid = $C_8H_4O_{10},KO,SbO_3$ solid ..... develops +4·1 Cal.

C. H. B.

Influence of Double- and Ring-linking on Molecular Volumes. By A. Horstmann (*Ber.*, **20**, 766—781).—In this paper, the author has brought together and classified in numerous tables the values obtained by various investigators for the molecular volumes (both at 0° and at the boiling point) of such substances as seemed likely to throw light on the influence of molecular structure on the molecular volumes of organic compounds.

Comparing compounds with open carbon-chains, the author finds that when a double linking is converted into a single linking by the addition of two atoms of hydrogen, the molecular volume increases, the increase at 0° varying from 4·1 to 9·4, the mean increase being 6·4. The instances taken include the conversion of unsaturated into saturated compounds, as well as of highly unsaturated compounds into less unsaturated (such as diallyl into hexylene). Most of the differences observed lie closely around the mean, 6·4.

Next, taking substances containing the benzene-ring and comparing their molecular volumes with those of their hexahydrides, the mean difference is found to be for $6H = 22·4$, or for $H_2 = 7·5$, or nearly the same as in the case of the open-chain formation. But when by a further addition of H_2 we pass from the hydrides of the aromatic compounds to fully saturated compounds the increase is much greater, the mean for H_2 being 16·2. This latter passage is of course accompanied with the change from the ring to the open formation. Similar results are shown between hydrides of aromatic compounds and their isomerides with open chains. In this case—where there is only difference of constitution and not of amount of hydrogen present—the molecular volumes of the compounds with open chains exceed those of the isomeric benzene compounds by about 8·5. Similar results are obtained by a comparison of compounds of the naphthalene series (containing two rings) with corresponding compounds of the aromatic and fatty series.

* These equations are given as in the original paper, O = 8.

Turning to the thiophen series, no such easy comparisons can be made since no hydrides are known. But comparing thiophen with diethyl sulphide, we find the molecular volume of the latter (107·6) to be 30·4 in excess of that of thiophen (77·2). Now here we have an addition of $3H_2$, a change of two double linkings to single ones, and of the ring to the open formation. Taking the numbers derived from the benzene series, we should obtain $(7·5 \times 2) + 16·5 = 31·5$, or almost exactly the difference found. Thus, although as we do not know the intermediate hydride we cannot speak with certainty, the numbers seem again in the thiophen series to point to a greater difference being caused by the addition of the two hydrogen-atoms which cause a breaking up of the ring formation, than is caused by a like addition when only a change from double to single linking takes place.

With regard to compounds containing nitrogen, we find in the fatty series that the conversion of nitriles to amines by the addition of $2H_2$, gives a mean increase of 11·8 or $2 \times 5·9$. In the case of pyridine-derivatives, comparison is more difficult, since the possible variation of mode of linking of the nitrogen-atom comes into consideration. But comparing the pyridine compounds with their hexahydrides we find the increase $3H_2 = 16·8$ or $3 \times 5·6$, and further comparing these hydrides with the corresponding amines of the fatty series we find the mean increase, $H_2 = 18·6$.

The above numbers all refer to molecular volumes determined at 0°. If those determined at the boiling point are employed, similar results are obtained, although of course the actual numbers are slightly different. In this case, the mean values are as follows:—I. Where the change is simply from double to single linking, H_2 in the fatty series = 7·1, in the aromatic series = 8·2, in the naphthalene series = 8·0, in the nitrogenous fatty series = 3·6, in the pyridine series = 6·5. II. Where the change is from the closed ring to the open chain $H_2 = 20·2$.

From the above results, the author draws the conclusion that "unsaturated compounds with ring formulæ have much smaller molecular volumes than their isomerides with open chains and polylinkings." He considers that in the present state of our knowledge of the subject, and absence of information as to the disturbing influences of other constitutional variations, no great stress should be laid on the actual numerical amounts of these differences, and that for the same reason it is also not well at present to attempt to calculate absolute values for the elements. The results obtained with compounds of the aromatic, thiophen, and pyridine series seem to speak in favour of Kekulé's ring formulæ. L. T. T.

Effect of Sulphuric Acid on the Solubility of Sulphates. By R. Engel (*Compt. rend.*, **104**, 506—508).—When sulphuric acid is added to solutions of sulphates which do not form acid salts, the solubility of the sulphate is diminished, but not in the same way as the solubility of chlorides in hydrochloric acid; that is to say, one equivalent of the acid does not precipitate one equivalent of the salt. The sulphuric acid behaves as if each molecule combined with

12 mols. of water and prevented them from exerting any solvent action. When the quantity of acid is very large, the divergences from this law become more marked. Details are given in the case of copper and cadmium sulphates. Other sulphates behave in a similar manner. The solubility of zinc sulphate is diminished by the first 12 equivalents of sulphuric acid, and it is only beyond this point that an acid salt begins to be formed. Magnesium sulphate and some others also show this phenomenon. C. H. B.

A Particular Case of Solution. By F. Parmentier (*Compt. rend.*, **104**, 686—688).—Crystallised phosphomolybdic acid containing 23·4 per cent. of water dissolves in ether with development of heat, but if excess of ether is then added, and the liquid agitated, the ether and the ethereal solution of the acid will not mix, but separate into two distinct layers. If the crystals were not dry, or if the ether was not really anhydrous, water separates as a third intermediate layer. When the ether is evaporated, the phosphomolybdic acid crystallises in the ordinary form. If the ethereal solution is separated from excess of ether, and heated in a sealed tube, a quantity of ether separates as a supernatant layer, the volume of which increases as the temperature rises. After cooling, the supernatant layer can again be mixed with the rest of the liquid, and a homogeneous fluid is obtained.

An ethereal solution of phosphomolybdic acid saturated at 13° has a sp. gr. of 1·3, and is soluble in alcohol in all proportions, but will not dissolve in water. If an aqueous solution of phosphomolybdic acid is agitated with ether, the whole of the acid is removed from the water, and the ethereal solution separates and sinks to the bottom. If the crystals of the acid are allowed to effloresce, or are heated at 100° for some time, they afterwards only dissolve in ether if a sufficient quantity of water is added.

The solubility of the acid in ether increases with the temperature, the quantity dissolved by 100 parts of ether being as follows:—

0°.	8·1°.	19·3°.	27·4°.	32·9°.
80·6	84·7	96·7	103·9	107·9

The solution of 1 kilo. of the acid in ether develops 22·8 Cal. or 90·2 Cal. per gram-molecule. A solution saturated with ether can dissolve large quantities of the acid with development of heat, but with separation of water as a supernatant layer. C. H. B.

Solubility of Calcium Orthobutyrate and Isobutyrate. By J. Chancel and F. Parmentier (*Compt. rend.*, **104**, 474—478).—Chatelier (Abstr., 1885, 340, 473) has deduced a relation between the heat of dissolution of a substance and its solubility, according to which, if dissolution takes place with absorption of heat, the solubility increases with a rise of temperature, and *vice versâ*. The authors have determined the solubility of normal calcium butyrate, which diminishes with a rise of temperature, and of calcium isobutyrate, which increases with a rise of temperature below 80°.

Calcium orthobutyrate forms nacreous lamellæ of the composition

$Ca(C_4H_7O_2)_2 + H_2O$, which do not lose their water below 130°. The solubility decreases gradually up to 60°, and then increases, the solubility at 100° being almost equal to that at 40°. The molecular heat of dissolution of its saturated solution in excess of water is +2·5, and hence the molecular heat of dissolution of calcium orthobutyrate to saturation is +5·8 Cal.

Calcium isobutyrate forms long prisms, which contain 5 mols. H_2O, and are very efflorescent. When heated at 100°, these crystals yield a hydrate containing 1 mol. H_2O, which forms thin lamellæ, resembling those of the ortho-salt, but efflorescent at the ordinary temperature. Its solubility increases gradually with the temperature up to 80°, and then diminishes, the value at 100° being the same as at 60°. The molecular heat of dissolution of the pentahydrated salt is +3·1 Cal.; the molecular heat of dissolution of its saturated solution is +2·5 Cal., and the difference (0·6 Cal.) is the molecular heat of solution of calcium isobutyrate to saturation. Hence, although the solubility of the salt increases with the temperature, it develops heat when dissolved to saturation. If the anhydrous salt had been used, this development would have been still greater.

It is evident from these facts that Chatelier's result cannot be regarded as a general law. C. H. B.

Laws of Solution: a Reply to Chancel and Parmentier. By H. Le Chatelier (*Compt. rend.*, **104**, 679—682).—Chancel and Parmentier's value for the heat of dissolution of calcium isobutyrate (preceding Abstract) is within the error of experiment. Calcium orthobutyrate obeys the author's law.

The sign of the heat of dissolution to saturation is readily determined by pouring a small quantity of water on an excess of the salt, and observing the movements of a thermometer placed in it, care being taken to avoid the presence of any effloresced crystals. The author finds in this way that the dissolution of calcium isobutyrate at the ordinary temperature produces a fall of temperature, whilst at 100° it produces a rise of temperature. The dissolution of the orthobutyrate is accompanied by a fall of temperature. In all cases the sign of the heat of dissolution is in agreement with the author's law.

The heat of dissolution of calcium isobutyrate which crystallises with at least 4 mols. H_2O above 80°, undergoes a sudden change of 3 cal. at this temperature, and it follows from the author's law that there should be a corresponding sudden change in the solubility. Chancel and Parmentier's results indicate the occurrence of such a variation at about 85°. C. H. B.

Coefficients of Chemical Affinity. By P. Chroustchoff and A. Martinoff (*Compt. rend.*, **104**, 571—574).—The authors have determined the composition of the precipitates formed by mixing dilute solutions of strontium chloride, barium chloride, and potassium sulphate, and barium chloride, potassium sulphate, and potassium chromate. The proportion of the different compounds in the precipitates varies with the order of mixing and the time during which the precipitate is left in contact with the liquid. Strontium sulphate

is completely converted into barium sulphate by contact with barium chloride solution for several hours. 12 per cent. of barium sulphate is converted into barium chromate by contact for 47 minutes with a solution containing potassium sulphate and potassium chromate in equivalent proportions, whilst 1·5 per cent. of barium chromate is converted into barium sulphate in the same time in contact with a similar solution. The limits of the reaction do not attain more than 22 per cent. and 17 per cent. respectively, even after 40 to 45 hours.

The initial composition of mixed precipitates formed by mixing salts in equivalent proportions approximates to a symmetrical distribution such that the precipitate contains 50 per cent. of each of the insoluble substances. The phenomenon of precipitation under these conditions is the result of the superposition of two distinct phases, the first of which is a purely mechanical initial distribution of all three substances according to the chances of their intermolecular encounters, whilst the second phase consists in a secondary (simultaneous or consecutive) transformation of the precipitates once formed by the action of the surrounding liquid. This secondary action takes place with a velocity which varies according to circumstances. Neither the initial nor the final composition of the precipitates serves to furnish coefficients of chemical affinity. C. H. B.

Inorganic Chemistry.

Compounds formed by the Action of Nitrous Acid on Sulphurous Acid. By F. Raschig (*Ber.*, **20**, 584—589).—The author states that the results of his investigation of the compounds formed by the action of nitrous acid on sulphurous acid, confirm those arrived at by Berglund (this Jour., 1876, ii, 44; 1877, ii, 111), but are at variance with those put forward by Claus and Koch (*ibid.*, 1871, 307, 659). Other compounds have been obtained in addition to those already known, and these form three series, which may be regarded as derived from the hydrate of nitrous acid, from the hypothetical dihydroxylamine, and from hydroxylamine, by the successive substitution of SO_3H for hydroxyl. They will be described later.

When an aqueous solution of hydroxylamine hydrochloride is saturated with sulphurous anhydride and afterwards evaporated, a large yield of amidosulphonic acid is obtained. W. P. W.

Carbonic Anhydride in the Air. By T. C. Van Nüys and B. F. Adams (*Amer. Chem. J.*, **9**, 64—66).—Eighteen estimations are given of the carbonic anhydride in air taken from University Park, Bloomington, one-half metre from the ground, and at 10 A.M. on different days in April. The average is 28·16 vols. per 100,000 vols. of air, the maximum 28·98, the minimum 27·34. Van Nüys' apparatus (Abstr., 1886, 835) was employed. H. B.

Vapour-density of Potassium Iodide. By J. Mensching and V. Meyer (*Ber.*, **20**, 582—583).—The authors have determined the vapour-density of potassium iodide in an atmosphere of nitrogen at a temperature of 1320°, and obtained in two experiments the values of 5·85 and 5·85, compared with 5·75, the density required by the formula KI. W. P. W.

New Hydrate of Sodium Hydroxide. By C. Göttig (*Ber.*, **20**, 543—544).—When a solution of sodium hydroxide in 96·8 per cent. alcohol of sp. gr. 0·935 is gradually heated to 25—30°, very slender, lustrous crystals slowly separate; these gradually disappear either on cooling or on further heating the solution. If the temperature is raised to 80°, the solution is almost clear, but as the solvent gradually evaporates a fresh separation of denser crystals occurs; these have the composition $NaHO + 2H_2O$. The new hydrate is not very hygroscopic, and readily absorbs carbonic anhydride; when thrown on to water, it swims about on the surface like sodium, and quickly dissolves. Its gives off a portion of its water of crystallisation in a desiccator over calcium chloride or sulphuric acid, loses about one-half at 120°, and is almost anhydrous at 220°. W. P. W.

Action of Metals on Solutions of Silver Nitrate. By J. B. Senderens (*Compt. rend.*, **104**, 504—506).—If pure sheet lead is placed in a solution of silver nitrate containing not more than 20 grams per litre, when one equivalent of lead has been dissolved, only about three-fourths of an equivalent of silver is precipitated. When all the silver has been precipitated, it is found that two equivalents of lead have been dissolved, and the solution contains lead nitroso-nitrate. If an excess of lead is left in the solution, the nitroso-nitrate is decomposed, and the reaction becomes complete when three equivalents of lead have been dissolved and tribasic lead nitrite has been formed.

The action of metallic lead on solutions of lead nitrate is very slow. Zinc, iron, tin, antimony and aluminium behave in a similar manner. In the case of zinc, nitrous oxide is given off together with a little nitrogen. The reaction is complete when four equivalents of zinc have undergone alteration, but only a small proportion of this passes into solution, the greater part remaining with the precipitated silver in the form of zinc hydroxide mixed with a little basic zinc nitrate. Under the same conditions, two equivalents of aluminium are altered with formation of the hydroxide and evolution of nitric oxide. A solution of zinc nitrate is not attacked by zinc in the cold, and aluminium is not attacked by nitric acid in the cold.

The decomposition of the nitrate and precipitation of the metal are correlated phenomena, and the precipitation of the silver determines the reduction of the acid radicle in the new salt. This reduction begins before the precipitation is complete, and continues simultaneously with the precipitation of the remainder of the silver.

C. H. B

Zinc-Eisen. By H. N. Warren (*Chem. News*, **55**, 100).—This alloy may be prepared in the following manner:—1 to 2 pounds

of zinc are melted in a clay crucible, 3 to 3½ ozs. of anhydrous sodium ferrous chloride are thrown in, and the crucible is immediately covered; violent reaction ensues, and the above alloy is produced. It is very brittle, has a full metallic lustre, and is easily pulverised.

D. A. L.

Ammonio-zinc Chlorides. By H. Thoms (*Ber.*, **20**, 743—744).—Compounds of the formula $ZnCl_2,NH_3$ and $ZnCl_2,5NH_3 + H_2O$, are already known. The author finds that if a stream of ammonia is passed into a hot concentrated solution of zinc chloride until the precipitate first formed is redissolved, and the whole is then allowed to cool, nacreous scales of the composition $ZnCl_2,4NH_3 + H_2O$ crystallise out. On concentration, the mother-liquor yields crystals of the formula $ZnCl_2,2NH_3$; this compound separates in colourless rhombic crystals, which do not change on exposure to air. It is insoluble in water, but when boiled with it decomposes with evolution of ammonia. It is easily soluble in solutions of ammonia or ammonium chloride. The same compound is also formed when ammonia is added to a cold dilute solution of zinc chloride until the precipitate first formed is redissolved, or when freshly precipitated zinc hydroxide is dissolved in a concentrated solution of ammonium chloride. The author has also found well-formed crystals of it in Leclanché cells. He considers the constitution to be expressed by the formula $NH_3Cl{\cdot}Zn{\cdot}NH_3Cl$.

L. T. T.

Cerite Earths. By E. Demarçay (*Compt. rend.*, **104**, 580).—The author has previously shown that the line 417 attributed to samarium, is not due to the substance which gives the line 400. Further experiments show that the line 417 is not due to the substance which gives the blue lines 480, 463, but at present there is no evidence that the lines 400, 480, 463 have a common origin.

The fractions obtained included some very rich in praseodidymium, and others which were free from this substance. The intermediate fractions showed the line 469 with an intensity equal to that of line 444. This line is attributed by Welsbach to praseodidymium, but its intensity in the intermediate fractions was very much greater than in the fractions consisting of almost pure praseodidymium, and it follows that this band is really due to some other substance. C. H. B.

Products from the Cowle's Electrical Furnace. By C. F. Mabery (*Amer. Chem. J.*, **9**, 11—15).—During the reduction of corundum a not inconsiderable amount of aluminium is volatilised, but this is prevented to a considerable extent by conducting the reduction in presence of heavy metals, such as copper, iron, or tin. The slag produced is principally an aluminate of calcium, formed from the lime used in preparing the charcoal lining of the furnace. The copper aluminium alloys contain 3—10 per cent. of crystalline silicon, and also calcium up to 3 per cent. Iron cannot be made to alloy with as large a proportion of aluminium as copper, usually the alloy contains only between 6 and 10 per cent., with 2·5 per cent. of silicon, and 2·5 to 3·7 per cent. of carbon. Such alloys possess valuable properties for foundry purposes, and are available for introducing aluminium into

steel. Sand is readily reduced, and copper will dissolve the silicon to the extent of 14 per cent.; the addition of small quantities of silicon increases the tensile strength of certain metals; thus the tensile strength of aluminium bronze (100,000 lbs. to the square inch) is increased to 120,000 lbs. by the addition of 1—2 per cent. of silicon. When silica alone is reduced, an amorphous greenish substance is found between the silicon and the silica; it is difficult to obtain pure, but from its mode of formation, properties, and the results of its analysis, is evidently *silicon monoxide*. H. B.

Action of Carbon Tetrachloride on Oxides. By L. Meyer (*Ber.*, **20**, 681—683).—When alumina is heated in a Glaser's furnace in a current of carbon tetrachloride (the air in the tube being first replaced by some dry indifferent gas), it is converted into aluminium chloride; carbonic anhydride, carbonic oxide, carbon oxychloride, and chlorine are formed in the reaction. The oxides of beryllium, magnesium, aluminium, and cerium are readily converted into the chlorides, whilst the anhydrides of boric, silicic, and titanic acids, and zirconia remain unchanged at the temperature of the Glaser furnace. The method is preferable to Oerstedt's for the preparation of such chlorides as volatilise with difficulty. N. H. M.

Preparation of Barium Manganate. By E. Donath (*Dingl. polyt. J.*, **263**, 246).—This green pigment is prepared by heating manganese carbonate with 2 to $2\frac{1}{2}$ times its weight of commercial barium dioxide in a porcelain crucible. A better green is obtained when well pulverised manganese dioxide (containing 91 per cent. of MnO_2) is heated with three times its weight of barium dioxide. D. B.

Formation of Manganates from Permanganates. By G. Rousseau (*Compt. rend.*, **104**, 786—788).—It is well known that when potassium permanganate is heated at 240° it splits up into potassium manganate, manganese dioxide, and oxygen. The author has found that if the heating is further prolonged, the manganese dioxide acts on the manganate with a velocity which increases with the temperature. The product consists of brownish-black microscopic crystals, which are very hygroscopic, owing to the presence of potassium oxide. After prolonged washing they have the composition of a heptamanganite, $7MnO_2,K_2O$.

The same compound is obtained in magnificent lamellæ when potassium permanganate is heated at 800° in a bath of potassium chloride. It is only formed out of contact with air, but is very stable, and is not decomposed in the oxidising flame, even at a bright red heat.

The formation of the manganite may be explained in the following manner. The permanganate first decomposes into manganate, manganese dioxide, and oxygen, and the manganate and dioxide react, with formation of fresh permanganate, manganese dioxide, and potassium oxide: $MnO_2 + 3K_2MnO_4 = K_2Mn_2O_8 + 2MnO_2 + 2K_2O$. The permanganate decomposes as before, and the same cycle of changes takes place, with a gradual increase in the amount of manganite and

free alkali, and a destruction of manganate and permanganate. These facts also explain the somewhat frequent failures in the preparation of the manganate. If the temperature is too high, reaction takes place between the manganate and the excess of dioxide.

Barium permanganate decomposes in a similar manner at 320°. If decomposition takes place in a closed vessel, the product is a dimanganite, $2MnO_2,BaO$, but if no precautions are taken to prevent access of moist air, the product is a heptamanganite, $7MnO_2,BaO$. Strontium and calcium permanganates behave similarly.

According to unpublished experiments of G. Lallement, metallic permanganates are converted into manganites at 100—150°. It is probable, therefore, that the method described is a general method for the preparation of metallic manganites. C. H. B.

Non-existence of Chromium Heptasulphide. By G. Bender (*Ber.*, **20**, 726—728).—The author attempted to prepare chromium heptasulphide by the method employed by Phipson (*Chem. News*, **4**, 125), and also by varying the conditions as much as possible, but obtained a mixed product containing less than half the amount of sulphur which would be contained in a heptasulphide. N. H. M.

Lower Oxides of Molybdenum. By W. Muthmann (*Annalen*, **238**, 108—137).—The preparation of *molybdenum dioxide* has been described by Svanberg and Struve (*J. pr. Chem.*, **44**, 257) and by Ullik (*Annalen*, **144**, 227). It is conveniently obtained by fusing a mixture of anhydrous ammonium molybdate (8 grams), molybdic acid (7 grams), calcined potassium carbonate (14 grams), and boric acid (7 grams).

Molybdenum dioxide molybdate, Mo_5O_{12}, first described by Berlin, is prepared by heating a mixture of ammonium molybdate (1 part) and molybdic acid (2 parts). The product is repeatedly extracted with ammonia, and finally with strong hydrochloric acid, to remove a compound of molybdenum and nitrogen. This oxide is not attacked by alkalis, but it dissolves in warm strong sulphuric acid, forming a green solution, which easily parts with sulphurous anhydride, and turns blue. Nitric acid, aqua regia, and chlorine-water convert Mo_5O_{12} into the trioxide.

The blue oxide of molybdenum, which is formed by the action of reducing agents on solutions of molybdic acid, or by boiling molybdenum-sulphuric acid, MoO_3,SO_3, with metallic molybdenum, has the composition Mo_3O_8. The olive-green oxide described by Berzelius appears to be a mixture of Mo_3O_8 and the hydroxide $Mo(OH)_4$.

When molybdenum is dissolved in strong sulphuric acid, the dioxide is first formed, which oxidises to molybdic acid. The molybdic acid combines with the dioxide, forming Mo_5O_{12}. At a higher temperature sulphur dioxide is given off, and Mo_3O_8 and MoO_3 are formed.

A dark-grey powder of the composition $Zn_2Mo_3O_8$ is formed by fusing sodium trimolybdate with metallic zinc. A similar magnesium compound has also been prepared. W. C. W.

Chlorostannic (Hydrochlorostannic) Acid. By K. Seubert (*Ber.*, **20**, 793—794).—Engel has described (Abstr., 1886, 984) a compound, $H_2SnCl_6 + 6H_2O$, under the above name. The author, in conjunction with Schürmann, has also independently obtained the same compound. He states that the best and easiest means of preparing it is as follows:—Stannic chloride is mixed with concentrated pure hydrochloric acid in such proportions that the water in the acid shall be in relation to the stannic chloride as $SnCl_4 : 6H_2O$. 100 parts of stannic chloride require 62·15 parts of 33 per cent. hydrochloric acid. Combination ensues, the mass becomes hot and softens, and hydrogen chloride is evolved. About 8 parts more of dry hydrogen chloride are then slowly passed into the mixture, which is then cooled. The whole solidifies to a scaly crystalline mass of the pure acid. The author gives the melting point of the pure substance as 19·2°. L. T. T.

Bromostannic (Hydrobromostannic) Acid. By K. Seubert and Schürmann (*Ber.*, 794—796).—The authors have obtained this compound in a way analogous to that employed (see preceding Abstract) for the preparation of the corresponding chloro-compound. 100 parts of melted stannic bromide were mixed with 74·1 parts of 50 per cent. hydrobromic acid. These proportions contain the necessary constituents for the formation of the compound $H_2SnBr_6 + 9H_2O$. The two liquids gradually mix, assume an amber colour, and the liquid gradually solidifies, leaving but very little mother-liquor. The pure substance crystallises in amber-coloured needles or triclinic plates, and melts at 47°. It is very deliquescent, and evolves hydrogen bromide when exposed to the air, making its analysis very difficult. The analyses agree most closely with the formula $H_2SnBr_6 + 7H_2O$, but from analogy with the corresponding platino-compound the authors are inclined to believe the composition to be more probably $H_2SnBr_6 + 9H_2O$. The *sodium salt*, $Na_2SnBr_6 + 6H_2O$, obtained by adding sodium carbonate to a solution of the acid, forms transparent, yellow needles. It is easily soluble in water, effloresces in the air, and at 90° loses all its water and stannic bromide.

L. T. T.

Gold. Part II. By G. Krüss (*Annalen*, **238**, 30—77; compare this vol., p. 340).—The author reviews the various determinations of the atomic weight of gold which have been made from time to time by different chemists. For the purposes of this research, the purest refined gold of commerce was dissolved in aqua regia, evaporated to dryness with hydrochloric acid, and the residue redissolved and diluted with a large volume of water to precipitate the silver chloride dissolved by the acid liquid. The solution of auric chloride was further purified by one of the following methods:—I. The metal is precipitated by sulphurous acid, washed with hydrochloric acid and water, dried at 180°, and digested with strong sulphuric acid in a platinum dish to remove traces of silver. The residue is washed in hot water, dried, and fused in a platinum dish with potassium hydrogen sulphate to remove palladium, and afterwards fused with potassium

nitrate to remove iridium. Finally the gold is redissolved in aqua regia and reprecipitated by sulphurous acid. In methods II and III the gold is precipitated from the dilute solution of auric chloride by oxalic acid or ferrous chloride instead of sulphurous acid. IV. The gold is precipitated by ferrous chloride and purified as in method I; the metal is dissolved in aqua regia and reprecipitated by sulphurous acid. It is again dissolved, and finally precipitated by means of oxalic acid.

The author has mapped out the spark spectrum of gold; his results agree fairly well with those of L. de Boisbaudran (*Spectres Lumineux*, Paris, 1874), with the exception that six lines, of wave-lengths 560·1, 522·8, 521, 444·2, 434·5, 406·2, are missing. These lines observed by Boisbaudran are due to the presence of traces of platinum, palladium, and nitrogen. The temperature of the prism exerts a considerable influence on the position which the bright bands of the spectra occupy. Gold can be quantitatively separated from ruthenium, rhodium, and iridium by means of ferrous chloride, oxalic, or sulphurous acid. The separation of gold from platinum is best effected by oxalic acid, and from palladium by sulphurous acid.

W. C. W.

Mineralogical Chemistry.

New Zealand Graphite. By R. W. E. McIvor (*Chem. News*, **55**, 125).—Two samples of graphite from Pakawan Bay, in Golden Bay, New Zealand, when dried, contained per cent.—

Carbon	34·99	51·45
Ash.....	65·01	48·55

D. A. L.

Natural Solutions of Cinnabar, Gold, and Associated Sulphides. By G. F. Becker (*Amer. J. Sci.*, **33**, 199—210).—In the course of investigations on the geology of the quicksilver deposits of California, the author has taken up the question of the state of combination in which mercury is dissolved in natural waters. His experiments show that there is a series of mercury compounds of the form HgS,nNa_2S, one or the other of which is soluble in aqueous solutions of sodium hydroxide, hydrosulphide, or sulphide, and apparently also in pure water at various temperatures. These solutions subsist in the presence of sodium carbonates, borates, and chlorides. The waters of Steamboat Springs and of Sulphur Bank contain mercury in this form. Iron disulphide, gold, and zinc blende readily dissolve in sodium sulphide, and form double sulphides with sodium analogous to those of mercury. Copper also forms a soluble double sulphide, but combines more readily with sodium hydrosulphide than with the simple sulphide. All these soluble sulpho-salts may exist in the presence of sodium carbonate. Mercuric sulphide is readily precipitated from these solutions, diminishing temperature and pressure

being causes of precipitation. There are other natural methods of precipitation. Thus, mercury is precipitated by strong solutions of borax or hydrogen sulphide, or any stronger acid. At Steamboat Springs and Sulphur Bank, sulphuric acid is formed near the surface, and, percolating downward, precipitates mercury. Other ores and gold must be precipitated by the same causes. Another method by which mercury sulphide may be precipitated is mere dilution. This precipitation is accompanied by the formation of thiosulphate, a salt actually occurring in the waters of Steamboat Springs.

The conditions of the solution and precipitation of ores described by the author are undoubtedly mainly instrumental in forming the deposits of Steamboat Springs and Sulphur Bank. Most of the other Californian quicksilver mines show similar ores and gangue minerals, and many of them are accompanied by warm springs, containing much the same salts in solution. Some of the gold deposits bear so close a resemblance to these deposits as to indicate that they also were formed by precipitation from solutions of soluble double sulphides.

B. H. B.

Artificial Formation of Rubies. By Fremy (*Compt. rend.*, **104**, 737—738).—The methods employed by the author and Feil in 1877 for the artificial preparation of rubies were—(1) To heat to bright redness in a fireclay crucible a mixture of alumina and red lead, with a minute quantity of potassium dichromate; and (2) to heat to a high temperature equal weights of alumina and barium fluoride with traces of potassium dichromate. The crystals were remarkable for their distinct shape, but were frequently lamellar. C. H. B.

Action of Fluorides on Alumina. By Fremy and Verneuil (*Compt. rend.*, **102**, 738—740).—The silica of the clay crucibles formerly used for the artificial preparation of rubies had no influence on the result, since the same effect is obtained in platinum or aluminium crucibles.

Almost all fluorides bring about the crystallisation of alumina at a red heat, but the experiments have been mainly confined to barium fluoride, calcium fluoride, and cryolite. When calcium fluoride and alumina are heated together in a platinum crucible at a very high temperature, a relatively small quantity of the fluoride exerts a very great mineralising power on the alumina. A mixture of 12 parts of alumina with 1 part of calcium fluoride becomes completely crystalline.

At the bottom of a platinum crucible, a layer of very pure transparent white fluorspar was placed, and on this a sheet of platinum pierced with minute holes. A thick layer of alumina, obtained by the calcination of ammonia alum and previously mixed with a minute quantity of chromic anhydride, was then added, and the crucible and its contents were heated to bright redness for several hours in a clay crucible, brasqued with alumina. After cooling, it was found that the calcium fluoride had fused, and the whole of the alumina was converted into crystals remarkable for their rose colour and their distinct form.

Many fluorides, when heated in contact with moisture, evolve hydrogen fluoride, which can effect the crystallisation of amorphous

substances, like alumina. It is, therefore, reasonable to suppose that hydrofluoric acid at a high temperature has played an important part as a mineralising agent.

The crystals obtained in this way are too small to have any commercial value. C. H. B.

Zinc Ferrite: Artificial Production of Franklinite. By A. Gorgeu (*Compt. rend.*, **104**, 580—583).—A solution of sodium sulphate (1 mol.), of zinc sulphate (1—2 mols.), and of ferric sulphate (0·25—0·5 mol.), was evaporated to dryness, and fused at a cherry-red heat, a small quantity of the mixture being removed from time to time and treated with boiling water. When nothing but octahedra were seen in the liquid, together with some basic zinc sulphate, fusion was stopped, and the cooled mass was extracted with boiling water, the basic zinc sulphate being removed by means of dilute acetic acid.

The formation of zinc ferrite under these conditions is due to the action of the ferric oxide, formed by the decomposition of the ferric sulphate, on the mixture of sodium sulphate and basic zinc sulphate. The ferrite can in fact also be obtained by the action of powdered hæmatite on a mixture of zinc and sodium sulphates, fused at a cherry-red heat. If the hæmatite contains sand, crystals of willemite appear after the formation of franklinite, and before the formation of crystallised zinc oxide. This fact assists in explaining the association of these three minerals in certain veins.

Franklinite can also be formed from zinc chloride or fluoride. The chloride is heated in moist air with ferric chloride, or with powdered hæmatite. In the case of the fluoride, 4 parts are mixed with 6 parts of potassium fluoride, and 2 parts of ferric fluoride or 1 part of ferric oxide. Any crystals of zincite which are formed are removed by treatment with dilute acetic acid.

Franklinite obtained by these methods crystallises in regular octahedra, modified by facets of the rhomboidal dodecahedron. Small crystals are transparent, have a reddish-brown colour, and are monorefractive; larger crystals are opaque, and have a metallic lustre. They are not magnetic, are not affected by heat, and are only very slowly attacked by acids; hardness, 6·5; sp. gr. 5·33.

Natural crystals of franklinite are opaque, and give a brownish-black streak, whilst the streak of the artificial product is yellowish-red. Moreover the natural mineral is magnetic, and its sp. gr. does not exceed 5·09. These differences are due to impurities in the natural mineral. A franklinite identical with the natural mineral is obtained by fusing together sodium sulphate and 10 per cent. each of zinc, manganese, and ferric sulphates, and adding a small quantity of a reducing agent, such as ferrous sulphide, during fusion. The small quantity of ferrous oxide thus formed combines with some of the ferric oxide and forms magnetite, which crystallises with the zinc ferrite. C. H. B.

Plumbocalcite from Wanlock Head. By A. Lacroix (*Jahrb. f. Min.*, 1887, Ref., **1**, 238—239).—Five varieties of plumbocalcite from Wanlock Head, Scotland, had the following composition:—

	I.	II.	III.	IV.	V.
$PbCO_3$	9·5	3·1	2·7	3·5	8·2
$CaCO_3$.....	90·5	96·9	97·3	96·5	91·8
Sp. gr.	2·74	2·72	2·72	2·73	2·74

B. H. B.

Phosphoric Acid in Chili Saltpetre. By C. Ochsenius (*Jahrb. f. Min.*, 1887, **1**, Mem., 221—222).—The principal argument always brought forward against the theory of the formation of Chili saltpetre from guano, was that no phosphoric acid could be detected in the nitrate. The ordinary analytical methods give only negative results. The author has carefully examined a series of strata from the nitrate beds of Taltal, in the Chilian province of Atacama. He employed Streng's microchemical method, and obtained the unmistakable green rhombic dodecahedra of molybdenum-ammonium phosphate in the specimens from the beds above the nitrate deposit, and in the ordinary sodium saltpetre. No phosphoric acid could, however, be detected in the white, crystalline nitrate, or in the beds below the deposit.

B. H. B.

Some Chilian Alums. By L. Darapsky (*Jahrb. f. Min.*, 1887, **1**, Mem., 125—137).—1. *Stüvenite.*—An alum found in some abandoned workings at the Alcaparrossa Mine, near Copiapó, gave on analysis the following results :—

H_2O.	SO_3.	Al_2O_3.	MgO.	Na_2O.	K_2O.	Total.
47·6	36·1	11·6	1·0	2·7	trace	99·0

The formula is—

$$Na_2O,SO_3 + MgO,SO_3 + 2(Al_2O_3,3SO_3) + 48H_2O.$$

For this well-characterised species the author proposes the name of *stüvenite*, in honour of Enrique Stüven.

2. *Sesqui-magnesia alum.*—Pure aluminium sulphate occurs frequently in Peru (see Field, this Journal, 1869, 259). A specimen from Cerros Pintados, in the National Museum of Santiago, only partially agrees with the descriptions hitherto published. In places, the mineral was considerably altered on the surface. When broken, however, it exhibited the remarkable fibrous character that occurs so frequently in all halotrichites. At one end of the specimen, the fibres pass into a pale pink crystalline mass. Analysis gave the following results :—

	MgCl.	Al_2O_3.	MgO.	SO_3.	H_2O.	Insol. res.
I.	0·24	11·60	5·82	35·95	45·97	0·36
II.	0·14	10·26	6·90	35·17	48·54	—
III.	1·07	8·29	4·19	25·65	36·13	—

I. Massive alum. II. Fibrous alum. III. Weathered powder. The formula of the massive alum is $2MgO,SO_3 + Al_2O_3,3SO_3 + 28H_2O$, or that of picroalumogene. The formula of the fibrous alum, $3MgO,SO_3 + 2Al_2O_3,3SO_3 + 53H_2O$, represents a sesqui-magnesia alum.

B. H. B.

Cristobalite from Mexico. By G. vom Rath (*Jahrb. f. Min.*, 1887, **1**, Mem., 198—199).—Near the summit of the Cerro S. Cristóbal, near Pachuca, in Mexico, the author found some white, regular crystals associated with tridymite. Their hardness was 6—7, and their sp. gr. 2·27. Analysis of a minute quantity gave the following results:—

SiO_2.	Fe_2O_3 with some Al_2O_3.	Total.
91·0	6 2	97·2

These regular crystals consist essentially of silica. The question then arises, are the crystals pseudomorphs, or do they represent a new octahedral form of silica? This can only be solved by collecting further material. Should it be desirable to give a name to this mineral, the author suggests that of *cristobalite*, from the locality where it was found. B. H. B.

Artificial Production of Quartz and Tridymite. By K. de Chroustchoff (*Jahrb. f. Min.*, 1887, **1**, Mem., 205—208).—In 1870, the author artificially formed for the first time the two crystallised modifications of silica. The crystals were, however, quite microscopic in character. He has recently succeeded in forming quartz in the wet way, and tridymite in the dry way. The products obtained are of remarkable beauty, finely developed columns of quartz with the two rhombohedra, and almost pure tridymite, the size of a bean.

For the artificial production of quartz the author employed an aqueous solution of silicic acid (dialysed silica). Several quarter litre glass bulbs, 0·5 cm. thick, were half filled with a 10 per cent. aqueous solution of silica, and heated at 250° in an air-bath for several months. During the first day the silica separated out. In six months' time hard sandy grains were found in the white precipitate. These were collected and washed, and were found to consist of transparent, colourless, homogeneous, well-developed crystals of quartz, 0·5 mm. in size.

In preparing tridymite artificially, the natural process was imitated, that is, by means of molten magmas artificial frittings were effected. Two series of experiments were conducted:—1. Rocks rich in quartz were melted with basalts or melaphyres, and kept in the molten state for 1 to 8 hours. 2. Rocks rich in quartz were fritted or quite melted alone in a charcoal coke fire. Both series of experiments yielded excellent specimens of tridymite. B. H. B.

Artificial Production of Crystallised Silica and Orthoclase. By K. de Chroustchoff (*Compt. rend.*, **104**, 602—603).—In part a description of the results given in the preceding Abstract. One of the quartz crystals showed several very small cavities with movable globules.

In other experiments the solution of dialysed silica was mixed with a small quantity of dialysed alumina and of potassium hydroxide, the mixture being heated in flasks at 300° for several months. Under these conditions crystals of quartz similar to those formed in the first experiments were obtained, mixed with a small quantity of thin

rhombic lamellæ, with the same properties as the adularian orthoclase obtained by Friedel and Sarasin. C. H. B.

Composition of Felspars in the Island of Elba. By A. Funaro (*Gazzetta*, **16**, 523—526).—It is generally held by geologists that the quartziferous porphyry of Elba is a structural variety of the granite in that island, the difference being dependent on variations in consolidations of the original magma. This view is supported by the following analyses, which indicate no marked difference in the chemical composition of these two species of rock. I. Granite. II. Gneissic schist. III. Quartziferous porphyry: —

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.
I.	69·3	16·4	4·5	1·12	1·18	3·46	5·02
II.	75·5	11·85	4·55	0·56	1·08	3·97	2·41
III.	70·1	16·25	4·05	1·32	0·54	4·2	4·27

With the analysis of the granite that of the gneissic schist is also compared, from which it appears that the composition of these rocks is very similar; the greatest difference is evident in the proportion of the silica. This result offers some confirmation of the view of geologists that granite is formed from gneiss and other more or less felspathic schists. Probably boron was present in minute quantities in the three species of rocks above described. V. H. V.

The Scapolite Series. By G. Tschermak (*Jahrb. f. Min.*, 1887, **1**, Ref., 232—234).—The author submits the arguments brought forward by Rammelsberg (Abstr., 1886, 30 and 318) to severe criticism, and adheres to his theory that the members of the scapolite group are admixtures in different proportions of the two species meionite and marialite. The differences between the results of actual analyses of scapolite minerals and the theoretical results found by calculation, are quite insignificant. In conclusion, the author gives the following table, showing the calculated percentage compositions of the scapolite mixtures:—

Meionite.	Marialite.	SiO_2.	Al_2O_3.	CaO.	Na_2O.	Cl.
100	0	40·45	34·38	25·17	—	—
90	10	42·80	32·75	22·65	1·47	0·42
80	20	45·15	31·13	20·13	2·94	0·84
70	30	47·50	29·50	17·62	4·40	1·26
60	40	49·85	27·88	15·10	5·87	1·68
50	50	52·20	26·25	12·59	7·34	2·10
40	60	54·55	24·62	10·07	8·81	2·52
30	70	56·90	23·00	7·55	10·28	2·93
20	80	59·25	21·37	5·03	11·75	3·35
10	90	61·60	19·74	2·52	13·22	3·77
0	100	63·95	18·12	—	14·69	4·19

B. H. B.

Artificial Production of Micas. By P. Hautefeuille and L. P. de Saint-Gilles (*Compt. rend.*, **104**, 508—510).—A mixture of

5 parts of the constituents of a highly ferruginous mica with 1 part of potassium silicofluoride melts between 1000° and a bright red heat, and loses fluorine somewhat rapidly in the form of silicon fluoride. If the mixture is allowed to crystallise whilst the proportion of fluorine remaining is still considerable, the solidified mass is more or less vesicular, but if the temperature is regulated so that crystallisation takes place when about 3 or 4 per cent. of fluorine is present, the product crystallises in the same form as mica, and has a similar composition. It forms thin pseudohexagonal plates, which are striated and macled, show polychroism, and melt before the blowpipe with intumescence. The crystals resemble the ferruginous mica of eruptive rocks, but have a slighter lower specific gravity, and are somewhat harder, but less elastic. These properties are well shown by magnetic crystals, which resemble the ferruginous micas of Vesuvius, and have the composition $6RO,2R_2O_3,9SiO_2$. By reducing the proportion of magnesia, crystals are obtained of the composition $4RO,2R_2O_3,9SiO_2$, which closely approaches that of chromium mica. These crystals are harder and less elastic than those of mica. In some cases the increased hardness and diminished elasticity are due to admixture with a hard vitreous substance.

The formation of crystallised minerals is facilitated by adding 10 per cent. of potassium arsenate to the fluorine-containing mixtures. If the silicate is allowed to solidify in an atmosphere of hydrogen, the product retains very little arsenic. The action of this gas produces intumescence, which facilitates the formation of geodes, and the latter contain crystals as much as 2 or 3 mm. in length.

C. H. B.

Talc, Pseudomorphite, and Muscovite from South Africa. By E. Cohen (*Jahrb. f. Min.*, 1887, **1**, Mem., 119—124).—The substances carved by the natives of South Africa are not only interesting ethnographically, but also mineralogically. They are found on investigation to be massive varieties of talc, chlorite, and muscovite.

The talc is of a light grey colour with yellowish-brown streaks. Its sp. gr. is 2·794. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
63·29	1·24	0·16	4·68	27·13	4·40	100·90

The pseudophite was obtained from the Zoutpans Mountains in the Northern Transvaal. It closely resembles williamsite (serpentine). Its hardness, however, is less (2—3), and it fuses more easily. Analysis gave the following results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
32·38	18·79	0·80	2·39	31·64	14·15	100·15

Of the water, 0·06 per cent. was given off between 100° and 300°, the remainder on ignition. The sp. gr. is 2·647.

The hardness of all the varieties of massive muscovite examined is from $2\frac{1}{2}$ to 3. Analyses are given of a green variety with green and brown streaks (I), a yellow variety with yellow-ochre streaks (II), and a red variety, with brown and violet streaks (III) :—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.
I.	45·39	0·98	38·72	0·61	—	0·45	0·17
II.	43·61	—	35·61	trace	trace	trace	0·79
III.	42·70	—	29·98	7·62	1·57	0·37	trace

	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	7·51	1·69	5·48	101·00	2·832
II.	—	—	7·00	—	2·847
III.	10·57	1·52	4·96	99·29	2·789

B. H. B.

Kersantite from Wüstewaltersdorf, in Silesia. By E. Dathe (*Jahrb. f. Min.*, 1887, **1**, Ref., 272—273).—The author has discovered a vein of kersantite in the culm beds at Wüstewaltersdorf, in Lower Silesia. The vein is 500 metres long and 80 to 100 metres broad. The principal constituents of the rock are plagioclase and magnesia-mica, with augite, hornblende, and quartz; whilst apatite, magnetite, and calcite occur as accessory or secondary minerals. An analysis of the rock gave the following results:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.
56·18	0·45	15·51	2·86	3·94	5·46	3·69	3·21	4·07

P_2O_5.	CO_2.	H_2O.	SO_3.	Total.	Sp. gr.
0·31	0·95	3·19	trace	99·82	2·7084

B. H. B.

Andalusite from Marabastad, Transvaal. By J. Götz (*Jahrb. f. Min.*, 1887, **1**, Mem., 211—212).—It has been stated that the andalusite in the ottrelite and andalusite schists of the Marabastad goldfields in the Transvaal, might be disthene. The author has consequently made a fresh investigation of the mineral in question. The sp. gr. he finds to be 3·11; that of distene is considerably greater. Analysis gave the following results:—

SiO_2.	Al_2O_3.	TiO_2.	Total.
28·38	56·50	15·14	100·02

The mineral cannot be disthene, on account of its specific gravity and the absence of perfect cleavage. B. H. B.

New Analyses of Norwegian Rocks. By P. Jannasch (*Ber.*, **20**, 167—176).—In 1855, T. Kjerulf published a number of analyses of the interesting rocks occurring in the vicinity of Christiania. The gaps in his series are now filled by new analyses, by the author, of rocks from the same district. The rock of most frequent occurrence has received various names, such as Christiania syenite, Drammen granite, and syenite porphyry. In all its modifications the soda felspar is in excess of the potassium felspar. It thus differs from the granites and syenites of the same age, and belongs to the group of rocks termed *prædacite* by Lang. It differs from the diorites and diabases in the constant proportion of primary quartz. The mineral constitution of the rock is very variable, the prevailing constituents being felspars, of which the author distinguishes three series differing in age. The typical rock is that from the Tonsen Aas (analysis II),

whilst that from Drammen (I) and that from Vettakollen (III) must be regarded as products altered by the eruption. In the typical rock, albite-oligoclase-perthite predominates; in the Vettakollen rock the plagioclases of the first generation, which were absent in the typical rock, also occur; whilst in the Drammen rock the albite-microcline and orthoclase-albite-perthites prevail.

Seeing that the Christiania prædacite has hitherto been erroneously regarded as an orthoclase-quartz rock, the interesting question arises whether orthoclase-quartz rocks, in which potash felspars are in excess of soda felspars, are altogether absent from the eruptive rocks of the Silurian basin of Christiania. No analysis of the Drammen porphyry has hitherto been published. That given below (analysis IV), together with the results of the microscopical examination, prove the porphyry to be a true potash-felspar rock. The percentage of the constituents of the rock calculated from analysis is as follows:—Orthoclase 42, albite 20, quartz 34, chlorite 2, iron pyrites 0·7, zircon 0·5, titaniferous iron ore 0·3.

	I.	II.	III.	IV.
SiO_2	76·05	64·04	59·56	75·44
TiO_2	0·05	0·62	1·22	0·07
ZrO_2	0·42		0·44	0·34
Al_2O_3	11·68	17·92	17·60	12·33
Fe_2O_3	0·34	0·96	2·90	0·49
FeO	1·05	2·08	3·38	1·00
MnO	trace	0·23	0·03	0·11
MgO	0·29	0·59	1·87	0·52
CaO	0·42	1·00	3·67	trace
FeS_2	—	—	—	0·66
Na_2O	3·79	6·67	4·88	2·38
K_2O	5·09	6·08	4·40	7·13
H_2O	1·36	1·18	1·37	1·26
Total	100·54	101·37	101·32	101·73
Sp. gr.	2·636	2·646	2·729	2·618

B. H. B.

Eruptive Rocks from Krzeszowice, near Cracow. By R. Zuber (*Jahrb. f. Min.*, 1887, **1**, Ref., 277—279).—The rocks are divided into two groups according to their petrographical character —syenite-porphyry, and melaphyre. The Zalas rock (analysis I) the author regards as syenite-porphyry. In this rock orthoclase occurs with plagioclase and biotite in a ground-mass of felspar, biotite, and hornblende. Near the surface the rock assumes a reddish colour, secondary quartz, hæmatite, and limonite occurring (analysis II). The dark-red rock occurring at Mienkinia, hitherto regarded as felsite-porphyry, is found by the author to be syenite-porphyry (analysis III). All the remaining eruptive rocks of the district are stated to be melaphyres. The rocks are sometimes compact, sometimes amygdaloidal. They consist of plagioclase, orthoclase, augite, and magnetite. Analyses are given of the rocks from Tenezyn (IV) and from Poçeba (V).

	I.	II.	III.	IV.	V.
SiO_2	59·82	68·45	65·82	54·93	50·63
Al_2O_3	17·89	12·40	15·94	17·73	15·59
Fe_2O_3	4·43	4·20	5·06	13·55	10·37
CaO	3·81	1·53	1·65	4·35	6·62
MgO	1·74	0·67	trace	0·80	3·03
MnO	trace	—	trace	trace	2·92
K_2O.....	6·21	5·91	6·17	2·89	4·98
Na_2O	4·27	4·36	3·54	4·94	4·96
Ignition	2·01	1·24	1·85	0·96	—
Total	100·18	98·76	100·03	100·15	99·10
Sp. gr.....	2·66	—	2·68	2·79	2·78

B. H. B.

Japanese Rocks. By B. Kotô (*Jahrb. f. Min.*, 1887, **1**, Ref., 285—287).—The author gives the results of a microscopic examination of various rocks collected in the provinces of Izu, Kai, and Kozuke. Analyses are given of the labradorite and pyroxene from the pyroxene-andesite of Tokio, plagioclase-basalt from Funabara, diabase from Hinazura Poss, Kai, pyroxene-andesites from Izu-San, Amagin-San, and Miôgi-San (Kozuke) (compare *Jour. Geol. Soc.*, **40**, 431—457).

B. H. B.

The Mazapil Meteoric Iron. By W. E. Hidden (*Amer. J. Sci.*, **33**, 221—226).—Only eight meteoric irons are recorded as having been seen to fall. To this short list the author adds a ninth. This meteorite was seen to fall near Mazapil, in the State of Zacatecas, Mexico, at 9 P.M. on November 27, 1885, during the periodical star shower of the Bielids. When received by the author, the meteorite weighed 3950 grams. Its present weight is 3864 grams. It is a flat irregular mass, having a smooth surface covered with deep depressions. Its greatest length is 175 mm., and its greatest width is 60 mm. The lines of crystalline structure are somewhat similar to those of the Rowton iron, and very unlike the Mexican irons. In appearance, the mass bears a remarkable resemblance to the Hraschina, Agram iron. An analysis of a small fragment of the new meteorite gave the following results:—

Fe.	Ni.	Co.	P.	Total.
91·26	7·84	0·65	0·30	100·05

B. H. B.

Meteorites from Kentucky and Mexico. By G. F. Kunz (*Amer. J. Sci.*, **33**, 228—235).—The author describes two new meteorites from Carroll Co., Kentucky, and Catorze, Mexico. The mass from Carroll Co. is especially interesting because it probably belongs to the same fall as the meteoric iron found on the altars of the Turner mounds, Little Miami Valley, Ohio. The Carroll Co. meteorite was found in 1880 at Eagle Station, about 60 miles from the mounds where Putnam found the meteoric iron and the ornaments made from it. The mass, which weighs 80 lbs., is almost square, measuring 19 cm. in thickness, 22 cm. in width, and 29 cm. in length. All the original crust has disappeared. The mass is largely made up

of fine yellow transparent olivine, resembling closely that of the Pallas iron. The meteorite belongs to the siderolites of Daubrée and to the pallasite-group. Its sp. gr. was found to be 4·41; the meteorite, like the Turner's mound and Atacama meteorites, consisting of three parts of olivine to one of iron. Analysis of the olivine gave the following results:—

SiO_2.	MgO.	FeO.	MnO + CoO.	Total.
37·90	41·65	19·66	0·42	99·63

The metallic portion gave on analysis the following results:—

Fe.	Ni.	Co.	P.	Olivine.	Chromite.	Total.
71·73	14·27	0·95	0·05	11·12	0·90	99·02

The balance is oxygen in the form of iron oxide, and undetermined constituents.

The Catorze mass, weighing 92 lbs., was found by a miner near Catorze, San Luis Potosi, Mexico, in 1885. It is 31·5 cm. long, 34·5 cm. wide, and 20 cm. thick. The iron belongs to Meunier's caillite-group, and shows the Widmanstätten lines very clearly. The sp. gr. was found to be 7·509. Analysis gave the following results:—

Fe.	Ni + Co.	P.	Scale insoluble in HNO_3.	Total.
90·09	9·07	0·24	0·60	100·00

B. H. B.

Organic Chemistry.

Action of Heat on Heptine. By A. Renard (*Compt. rend.*, **104**. 574—576).—Heptine, C_7H_{12}, boiling at 103—105° was allowed to fall drop by drop into an iron tube which was heated to incipient redness, and was connected at the opposite end with a condensing arrangement. The products are a considerable volume of hydrogen mixed with a small quantity of gaseous hydrocarbons, a small quantity of carbon, and a large proportion of a brownish-yellow liquid which contains a small quantity of pentine, a large proportion of hexine, a small proportion of benzene, and a much larger proportion of toluene. This liquid also contains a considerable fraction boiling above 115°, about half of which boils between 115° and 180°, leaving a viscous residue which is solid at ordinary temperatures. This fraction has not been examined in detail, but it contains no hydrocarbons of the benzene series.

The pentine is either identical or isomeric with the pentine obtained by Greville Williams by the distillation of caoutchouc, or by Tilden in the pyrogenation of terebenthene.

Hexine, C_6H_{10}, the lower homologue of heptine, boils at 70—73°, and is soluble in alcohol, ether, and acetic acid; vapour-density, 2·97. It

rapidly absorbs oxygen, but exerts no action on ammoniacal cuprous chloride or ammonio-silver nitrate. It is violently attacked by bromine with evolution of hydrogen bromide, but if its ethereal solution is treated with bromine it yields the additive product $C_6H_{10}Br_2$, which after the evaporation of the ether forms a heavy oil, but soon decomposes with evolution of hydrogen bromide. Ordinary nitric acid attacks the hydrocarbon violently, but acid of sp. gr. 1·15 acts more gradually with evolution of carbonic oxide and carbonic anhydride, but no nitrogen oxides, and formation of a solution of formic, acetic, oxalic, and succinic acids. Gaseous hydrogen chloride produces a deep blue coloration. Hexine does not, like heptine, form a crystallisable hydrate with water. In contact with sulphuric acid, it polymerises with development of heat, and when the supernatant layer is distilled it yields dihexine, $C_{12}H_{20}$, a colourless liquid which boils at 210—215°, does not alter in contact with the air, and is not attacked by sulphuric acid.

The principal products of the action of heat on heptine are hydrogen and toluene, together with smaller proportions of the lower homologues of heptine, pentine, and hexine. The benzene is doubtless a product of the decomposition of some of the hexine. C. H. B.

Bismuth Thiocyanate. By G. Bender (*Ber.*, **20**, 723—726).—Bismuth thiocyanate, $Bi(CNS)_3$, is prepared by treating bismuth hydroxide with very dilute hydrogen thiocyanate solution (sp. gr. = 1·006). The solution takes place very slowly, and a small quantity of a yellow substance separates, probably consisting of basic salts (Meitzendorf (*Ann. Phys. Chem.*, **56**, 63). The product is evaporated in a water-bath, when a red, amorphous substance separates; on cooling, pure bismuth thiocyanate separates in aggregates of rather large crystals mostly of a bright-orange colour, but also partly amber-coloured. The crystals are rhombic; $a : b : c = 0{\cdot}76134 : 1 : 0{\cdot}28423$. It is decomposed by cold water into a yellow, amorphous substance and a red solution; when heated at 80°, it also decomposes. Cold nitric acid dissolves it with a red colour; in a short time an evolution of gas takes place, and a clear solution is formed containing all the sulphur in the form of sulphuric acid. N. H. M.

Action of Potassium Permanganate on Dextrose in Neutral Solution. By A. Smolka (*Monatsh. Chem.*, **8**, 1—26).—When dextrose is boiled with excess of potassium permanganate, it is completely oxidised to water and carbonic anhydride with separation of a potassium hydromanganite, $KH_3Mn_4O_{10}$. With excess of permanganate in the cold the action is the same, a trace of oxalic acid, however, being also formed.

By successively decreasing the amount of potassium permanganate, and allowing the action to take place at the ordinary temperature, there are obtained, in addition to water and carbonic anhydride, oxalic acid and formic acid, or the two latter alone, and a quantity of dextrose remains unaltered, depending on the amount of oxidising agent employed. The permanganate is reduced, partly to manganic, and partly to manganous oxide. The relative amounts of the products

of oxidation are variable even with the same proportions of dextrose and permanganate, and appear to be dependent on the temperature and concentration of the solutions. G. H. M.

Compounds of Phenylhydrazine with the Sugars. By E. Fischer (*Ber.*, **20**, 821—834).—Previous experiments by the author have shown that those sugars which reduce Fehling's solution combine with phenylhydrazine to form crystalline compounds sparingly soluble in water (Abstr., 1885, 53). Thus dextrose or lævulose reacts with phenylhydrazine hydrochloride in presence of sodium acetate to form phenylglucosazone, $C_6H_{10}O_4(N_2HPh)_2$, a change probably to be explained by the intermediate formation of a dextrose (or lævulose) phenylhydrazine, which reacts with two molecules of phenylhydrazine to form phenylglucazone, thus: (1) $C_6H_{12}O_6 + PhN_2H_3 = C_6H_{12}O_5N_2HPh + H_2O$; and (2) $C_6H_{12}O_5N_2HPh + 2PhN_2H_3 = C_6H_{10}O_4(N_2HPh)_2 + NH_2Ph + NH_3 + H_2O$. The intermediate dextrose phenylhydrazine forms small, colourless crystals melting at 144—145°, soluble in hot water and alcohol, insoluble in chloroform and benzene. It is decomposed by acids into the hydrazine and dextrose together with humous substances; on reduction with zinc-dust and acetic acid, it yields aniline and a basic substance to be described later.

Similarly galactose forms *galactose phenylhydrazine*, crystallising in colourless needles melting at 158° (uncorr.), and phenylgalactosazone melting at 193—194°, and not at 182° as stated formerly.

Phenylsorbinazone, from sorbin and phenylhydrazine, crystallises in yellow needles melting at 164°; it was formerly described as a liquid.

Phenyllactosazone differs from the above azones by its greater solubility in hot water; it is insoluble in ether and benzene. In the course of its formation its anhydride, $C_{24}H_{30}N_4O_8$, is also obtained; this crystallises in yellow needles melting at 223—224°, insoluble in water, ether, and benzene.

Phenylmaltosazone crystallises in yellow needles sparingly soluble in water, more readily in alcohol.

It is further shown by means of the phenylhydrazine reaction that one of the products of the oxidation of mannitol with nitric acid, namely mannitose, is identical with lævulose, thus confirming Dafert's experiments. The other product combines with the hydrazine to form a substance, $C_{12}H_{18}N_2O_5$, melting at 188°, isomeric with dextrose phenylhydrazine, from which it is distinguished by its more sparing solubility in water.

In conclusion, it is remarked that a more precise definition of the word sugar is required, for in the text-books substances of the general formula $C_6H_{12}O_6$ are classed together, all possessing to a greater or less degree the common property of sweetness, yet differing most markedly in their chemical behaviour. V. H. V.

Action of Nitric Acid on Sugar. By E. Maumené (*Compt. rend.*, **104**, 511).—Boutroux's failure to obtain hexepic acid was due to the employment of too small a quantity of nitric acid. Hexepic acid is absolutely identical with oxygluconic acid. C. H. B.

Blue Iodide of Starch. By F. Mylius (*Ber.*, **20**, 688—695).—The analogy between iodide of starch and iodocholic acid (this vol., p. 606), is shown by the following facts: (1) Iodine solutions which colour starch contain either hydriodic acid or one of its salts; (2) the presence of substances, such as chlorine, which decompose hydriodic acid prevents the formation of iodide of starch; (3) silver solutions decolorise solution of iodide of starch—the colour is restored by adding potassium or hydrogen iodide; (4) an aqueous solution of iodine cannot colour starch blue; the blue colour appears at once when a trace of hydriodic acid or potassium iodide is added.

When starch is added to a solution of iodine and hydriodic acid containing sulphuric acid, iodide of starch separates: the amount of iodine and hydriodic acid which has been absorbed by the starch can be readily determined by titration. The results of several experiments show that the proportion of iodine absorbed to that of the hydriodic acid is 4 : 1, and it is probable that the resulting compound has the formula $(C_{24}H_{40}O_{20}I)_4,HI$. From this, the author concludes that the formula of starch is $C_{24}H_{40}O_{20}$, which is that ascribed to it by Pfeiffer and Tollens (Abstr., 1882, 490).

Iodide of starch dried in a vacuum appears to be anhydrous. The *barium compound* was analysed, and has probably the composition expressed by the formula $(C_{24}H_{40}O_{20}I)_8,BaI_2$. The *potassium* and *sodium compounds* are soluble, the *barium* and *zinc compounds* are insoluble. N. H. M.

Reduction of Aldoximes and Acetoximes. By H. Goldschmidt (*Ber.*, **20**, 728—730; compare this vol., p. 249).—Isopropylamine is prepared by reducing 3 grams of acetoxime dissolved in 30 c.c. alcohol with 160 grams of 2·5 per cent. sodium amalgam and 14 grams of glacial acetic acid at 40°. The product is diluted with water, treated with soda solution, and distilled, the vapour being passed into dilute hydrochloric acid.

Heptylamine and ethylamine are obtained in a similar manner from œnanthaldoxime and ethaldoxime.

Salicylamine is best prepared by reducing salicylaldoxime with zinc-dust and acetic acid.

Furfurylamine was prepared from furfuraldoxime (m. p. 89°); it is soluble in water and boils at 143° (under 730 mm. pressure). The *hydrochloride* crystallises in thin needles, and the platinochloride in gold-coloured, lustrous plates. N. H. M.

Action of Nitrous Acid on Acetone. By T. Sandmeyer (*Ber.*, **20**, 639—641).—When acetone is treated with an equal weight of liquid nitrous anhydride at a temperature below 30° until all blue colour has disappeared, and the product is afterwards shaken with small quantities of water, a yellow oil is obtained. This is heavier than, and moderately soluble in water, has a strong acid reaction, and decomposes after a time or when gently heated. It is probably *isonitrosodiacetone nitrate*, $NO_2O\cdot CMe_2\cdot C(COMe):NOH$. When heated with dilute hydrochloric acid, it is decomposed into isonitrosochloracetone, $COMe\cdot CCl:NOH$, together with a small quantity of hydro-

gen cyanide and acetone. On boiling a dilute aqueous solution of isonitrosodiacetone nitrate, a small quantity of a white, insoluble, feebly explosive compound separates, acetone and hydrogen cyanide distil over in small quantity, and there remains in the flask a solution containing pyruvic acid, ammonia and nitric acid.

Isonitrosochloracetone yields an *oxime*, OH·N:CMe·CCl:NOH, crystallising in small, white needles melting at 171° with decomposition. W. P. W.

Action of Potassium Hydroxide on a Mixture of Acetone and Chloroform. By R. Engel (*Compt. rend.*, **104**, 688—691).—By the action of solid potassium hydroxide on acetone and chloroform, Willgerodt obtained a compound, acetone-chloroform, $C_4H_7OCl_3$, together with a smaller quantity of two acids, $C_{11}H_{20}O_6$ and $C_7H_{14}O_4$. The author has obtained the acid $C_{11}H_{20}O_6$ as the principal product under the following conditions:—

Acetone and chloroform in equivalent proportions are mixed with an equal volume of alcohol cooled to 0°, and then mixed with alcoholic potash also cooled to 0°, and containing twice the quantity of potassium hydroxide required to remove the whole of the chlorine. Carbonic oxide is evolved, and there is considerable development of heat. The flask is carefully cooled in the early stages of the process, but towards the end of the reaction the temperature is raised to 60—70°. The product is acidified with hydrochloric acid, filtered, the precipitated potassium chloride washed with alcohol, the filtrate and washings mixed with water and agitated with ether. When the ethereal solution is distilled, it leaves a yellow aqueous liquid, which is converted into a lead salt and recrystallised. The majority of the salts form gummy masses, but the lead salt crystallises in prisms of the composition $PbC_{11}H_{18}O_6 + 2H_2O$ when its solution is evaporated in a dry vacuum. The free acid volatilises in a dry vacuum, and the lead salt shows a decided tendency to become basic. The zinc salt, $ZnC_{11}H_{18}O_6 + 2H_2O$, crystallises in needles which lose their water when carefully heated at 140°. Both salts melt at about 100°, and begin to decompose at 150°. The acid, $C_{11}H_{20}O_6$, is formed by the condensation of three molecules of acetone with fixation of two COOH groups and loss of one atom of oxygen. It may possibly have the constitution $CMe_2(COMe_2,COOH)_2$.

Other acids are formed in the reaction, and remain in the aqueous solution after agitation with ether. C. H. B.

Chloroformamide: Synthesis of Aromatic Acids. By L. Gattermann and G. Schmidt (*Ber.*, **20**, 858—862).—When dry carbonyl chloride is passed into ammonium chloride heated at 400°, chloroformamide distils over, and solidifies in long, broad needles melting at 50°, and distilling at 61—62°. This substance has a peculiarly disagreeable odour. On keeping, it forms cyamelide with elimination of hydrogen chloride. By water, as also by damp air, it is decomposed into carbonic anhydride and ammonium chloride. It reacts with the amines to form monosubstituted carbamides.

Chloroformamide may be used to effect the synthesis of aromatic

acids by means of the aluminium chloride reaction, in that it yields with the hydrocarbons or ethers amides of these acids. Thus if chloroformamide is mixed with a solution of toluene in carbon bisulphide, and aluminium chloride is added, the amide of paratoluic acid is produced. In the paper, this method of synthesis is illustrated in the case of cuminic, naphthoic, anisic, and veratric acids.

V. H. V.

Tertiary Trichlorobutyl Chloride and Ether. By C. Willgerodt and F. Dürr (*Ber.*, **20**, 539—540).—When solid acetone-chloroform is treated with phosphorus pentachloride at 100°, tertiary trichlorobutyl chloride and ether are obtained and can be separated by fractional distillation.

Tertiary trichlorobutyl ether, $O(CMe_2{\cdot}CCl_3)_2$, boils at about 156°, does not solidify in a freezing mixture, distils undecomposed with steam, and strongly attacks the mucous membrane.

Tertiary trichlorobutyl chloride, $CMe_2Cl{\cdot}CCl_3$, melts and boils at about 167°, has a powerful odour, is volatile with steam, and is soluble in most organic solvents, insoluble in water. W. P. W.

Substituted Acrylic and Propionic Acids. By C. F. Mabery (*Amer. Chem. J.*, **9**, 1—11).—*Bromotrichloropropionic acid*, $C_3H_2Cl_3BrO_2$, is prepared by passing chlorine into a cold chloroform solution of chlorobromacrylic acid, and is purified by recrystallisation from carbon bisulphide. It melts at 83—84°. The following salts are described:—$Ba(C_3HCl_3BrO_2)_2$, a gummy mass; $Ca(C_3HCl_3BrO_2)_2$ oblique prisms, and $KC_3HCl_3BrO_2 + 2H_2O$, rhombic plates.

Trichloracrylic acid, $C_3HCl_3O_2$, is obtained by treating the above acid with a slight excess of baryta-water in the cold. After recrystallisation from carbon bisulphide, it melts at 76°. Water at 20° dissolves 6 per cent. of the acid. The following salts are described:—$Ba(C_3Cl_3O_2)_2 + 3\frac{1}{2}H_2O$, needles; $Ca(C_3Cl_3O_2)_2 + 3\frac{1}{2}H_2O$, needles; $KC_3Cl_3O_2$, crystalline plates; and $AgC_3Cl_3O_2$, which may be crystallised from hot water.

It has been supposed (Beilstein) that the dichlor- and dibrom-acrylic acids are represented by the formula $CX_2{:}CH{\cdot}COOH$, and not $CHX{:}CX{\cdot}COOH$. This view is not supported by evidence (compare Hill, Abstr., 1881, 1030); it has been shown, however (*ibid.*, 1029), that the additive product of chlorine and α-dibrom-acrylic acid is essentially different from the additive product of bromine and α-dichloracrylic acid. On the assumption of the formula $CHX{:}CX{\cdot}COOH$ for the disubstituted acrylic acids, these two additive products should be identical. In order to confirm these results the two acids have been treated with baryta-water, and thus converted into the corresponding bromodichloracrylic acids. Both acids yield salts which appear to be identical. The following are described:—$Ba(C_3BrCl_2O_2)_2 + 3H_2O$; $Ca(C_3BrCl_2O_2)_2 + 4H_2O$; $KC_3BrCl_2O_2$; and $AgC_3BrCl_2O_2$; but the free acids differ somewhat, namely, that prepared from α-β-dichloracrylic acid melts at 85°, is dissolved by water at 20° to the extent of 2·6 per cent., and when heated with water melts before dissolving, but solidifies on cooling; that pre-

pared from α-β-dibromacrylic acid melts at 78—80°, is dissolved by water at 20° to the extent of 6·9 per cent., and with water it forms an oil which does not solidify at 0°.

The author explains the existence of these two bromodichloracrylic acids by supposing that in the treatment of α-β-dibromacrylic acid with chlorine the β-atom of bromine is substituted by chlorine, and the chlorine monobromide forms an additive product, so that two chlorine-atoms are united to the same carbon-atom (β) ; the tri-substituted acrylic acid prepared from α-β-dibromacrylic acid would thus be CCl_2 : CBr·COOH, while that from α-β-dichloracrylic acid is

CClBr : CCl·COOH. H. B.

Preparation of Calcium and Potassium Tartrates. By T. Gladysz (*Dingl. polyt. J.*, **263**, 98—99).—The author has patented a process for extracting tartaric acid from wine yeast and other substances containing tartaric acid, based on the following facts: —When calcium tartrate is treated with water, and sulphurous anhydride introduced at the ordinary temperature, the tartrate dissolves completely. On heating the solution at 90—100°, sulphurous anhydride escapes, and a crystalline precipitate of calcium tartrate separates. A similar result is obtained on treating hydrogen potassium tartrate with sulphurous anhydride, a solution of hydrogen potassium sulphite and free tartaric acid being formed in the cold, whilst on application of heat sulphurous anhydride is liberated. Moreover, on adding normal or hydrogen potassium tartrate to a solution of calcium sulphite in sulphurous acid, calcium tartrate is precipitated, and a solution of hydrogen potassium sulphite is obtained.

D. B.

Furfuraldehyde. By H. Schiff (*Ber.*, **20**, 540—542).—A mixture of equal volumes of xylidine and acetic acid to which some alcohol has been added can be used to detect traces of furfuraldehyde, the presence of which is rendered evident by the production of the red colour of furfuroxylidine; the test is so delicate that the amount of furfuraldehyde (about 1 per cent.) formed when 0·00005 gram of sugar is heated in a tube, can be detected by holding a slip of paper moistened with the solution in the fumes. The author finds that furfuraldehyde is formed in many culinary processes, and that it is present in very small quantities in tobacco smoke. Furfuraldehyde is also formed in very small quantities when guaiacum resin is distilled, and its formation is probably due to the presence of a trace of glucoside in the resin (Kosmann, *Jahresb.*, 1863, 557); also when calcium pyromucate is distilled either alone or with calcium formate, and when pyromucic and mucic acids are distilled. Furoïn and furil give the reaction when their vapours are exploded with air, and furfuraldehyde can be detected when furfurin and hydrofurfuramide are distilled in vessels containing air. The dry distillation of furanilino hydrochloride, of pyromucanilide, of cholic and meconic acids, and of fats and fatty acids is not accompanied with the production of furfuraldehyde. W. P. W.

Negative Nature of the Phenyl-group. By V. Meyer (*Ber.*, 20, 534—536).—When a CH- or CH_2-group occurs between two CO-groups in the constitutional formula of a compound, as, for example, in that of ethyl acetoacetate, it is known that each atom of hydrogen is displaceable by a metal; the author's investigations, carried on in conjunction with his pupils, appear to prove that this property is not affected when phenyl is substituted for one of the CO-groups, and in this preliminary communication the chief results as yet obtained are briefly given. The hydrogen of the methylene-group in deoxybenzoïn, $Ph{\cdot}CH_2{\cdot}CO{\cdot}Ph$, is displaceable by methyl, ethyl, butyl, and benzyl, and these derivatives crystallise well and yield characteristic compounds with hydroxylamine. Dibenzylketone yields a benzyl-derivative of high melting point. Ethyl phenylacetate, however, does not react under ordinary conditions. Benzyl cyanide, when treated with benzyl chloride and sodium ethoxide, yields a well-crystallised benzyl-derivative, $CH_2Ph{\cdot}CHPh{\cdot}CN$, which boils without decomposition. Ethyl dinitrophenylacetate forms a well-crystallised compound, $C_6H_3(NO_2)_2{\cdot}CH(COOMe){\cdot}N_2Ph$, with diazobenzene chloride.

The thiënyl-group exerts an influence in the molecule similar to that of phenyl: thus the ketone $C_4SH_3{\cdot}CO{\cdot}CH_2{\cdot}Ph$ (?) reacts easily, like deoxybenzoïn, and yields crystalline derivatives.

W. P. W.

Pyrogenic Reactions. By P. Ferko (*Ber.*, **20**, 660—664).—By passing dry ethylene through gently boiling benzene, and then through an iron tube 60 cm. long, heated in a Mermet's gas furnace until all the benzene (1½ litres) was used up, a crude product was obtained from which the following hydrocarbons were isolated:—Unchanged benzene (80 grams), cinnamene (17 grams), diphenyl (300 grams), phenanthrene (10 grams), anthracene (15 grams). No naphthalene was formed.

When 1½ litres of toluene are passed through the tube (a process which takes eight hours), the following products are formed:—Benzene (150 grams), toluene (180 grams), cinnamene (7 grams), naphthalene (40 grams), diphenyl (27 grams), phenanthrene (1·5 gram), anthracene (12 grams), and an oil boiling at 270—280° (10 grams). Toluene (1¼ litres) and ethylene yielded benzene (200 grams), toluene (160 grams), cinnamene (10 grams), anthracene (20 grams), oil boiling at 270—280° (13 grams).

Naphthalene alone yielded only dinaphthyl together with unchanged naphthalene. Naphthalene (900 grams) and ethylene yielded—unchanged naphthalene (400 grams), acenaphthene (0·5 gram), phenanthrene (1 gram), and dinaphthyl (125 grams).

Ethylbenzene (500 grams) yielded—benzene (75 grams), toluene (5 grams), unchanged substance (20 grams), cinnamene (10 grams), naphthalene (11 grams), diphenyl (3 grams), phenanthrene (13 grams), and anthracene (2 grams). Azobenzene yielded only a small product, from which benzene and diphenyl were isolated.

N. H. M.

Aromatic Lead Compounds. By A. Polis (*Ber.*, **20**, 716—722).—*Lead tetraphenyl*, $PbPh_4$, is prepared by boiling 500 grams of

finely powdered alloy of lead and sodium (containing 8 per cent. of sodium) with 500 grams of bromobenzene and 20 c.c. of ethyl acetate for 60 hours. The liquid portion of the product is poured off, the residue extracted with hot benzene; the solutions are then mixed, and the excess of bromobenzene and benzene distilled off in a vacuum. The residue is first recrystallised from benzene in presence of animal charcoal, and then several times from warm ether. It forms small, colourless needles which melt at 224—225°, and decompose at 270°. Sp. gr. = 1·5298 at 20°. It is very sparingly soluble in alcohol, ether, and glacial acetic acid, more soluble in benzene, chloroform, and carbon bisulphide. It burns in air with a smoky flame. When heated with hydrochloric acid at 230°, lead chloride and chlorobenzene are formed.

Lead diphenyl dinitrate, $PbPh_2(NO_3)_2 + 3H_2O$, is readily obtained by gradually adding lead tetraphenyl to boiling nitric acid (sp. gr. 1·4). The acid must be kept at its boiling point. It separates on cooling in small, lustrous plates, and is recrystallised from water made acid with nitric acid. It is rather readily soluble in water and in alcohol. It detonates when heated below its melting point. When boiled with water, the liquid remains turbid owing to the formation of a *basic salt*, $OH{\cdot}PbPh_2{\cdot}NO_3$; this is a white powder.

Lead diphenyl diiodide, $PbPh_2I_2$, is formed when a solution of iodine in chloroform is added to lead tetraphenyl also dissolved in chloroform. It separates in gold-coloured plates which melt at 101—103°. It is soluble in chloroform, benzene, and alcohol. The corresponding bromide is a white powder which decomposes before fusing.

Lead tetraparatolyl, $Pb(C_7H_7)_4$, is prepared similarly to the phenyl compound from 120 grams of parabromotoluene, 300 grams of alloy, 40 grams of toluene, and 4 c.c. of ethyl acetate. The heating is continued for 50 hours. It is crystallised successively from benzene and alcohol. It forms small, colourless needles which melt at 239—240°, and decompose at 254°; sp. gr. +1·4329 at 20°. It is more readily soluble than the phenyl compound in benzene, carbon bisulphide, and chloroform. N. H. M.

Sulphuric Acid as an Iodine-carrier. By G. S. Neumann (*Ber.*, **20**, 581—582).—When equimolecular proportions of iodobenzene and sulphuric acid are heated at 100° for some hours, a mixture of paradiiodobenzene, iodobenzenesulphonic acid and benzenesulphonic acid is obtained. Ortho- and para-iodotoluene under like conditions yield diiodotoluene and triiodotoluene; whilst ortho- and para-iodophenol yield diiodophenol when treated with sulphuric acid in the cold. W. P. W.

Tribromophenol. By A. Purgotti (*Gazzetta*, **16**, 526—531).—The *calcium*-derivative of tribromophenol crystallises in white, silky needles; the *ammonium*-derivative forms minute crystals, more soluble in cold water than in hot; the *silver*-derivative is a red, insoluble powder darkening rapidly on exposure; the *lead*- and *zinc*-derivatives are white precipitates, and the *copper*-derivative a violet powder, insoluble in water, soluble in ammonia. The *ethyl*-derivative crystallises in bril-

liant prisms melting at 69°. As an antiseptic, tribromophenol seems to be superior to phenol and thymol. V. H. V.

Manufacture of Resorcinol. By O. Mühlhäuser (*Dingl. polyt. J.*, **263**, 154—157).—This substance is prepared on a large scale by fusing sodium benzenedisulphonate with sodium hydroxide. Its production from benzene involves the following operations:—(1.) Preparation of benzenesulphonic acid by treating pure benzene free from thiophen with sulphuric acid of 67° B. (2.) Conversion of the monosulphonic acid into benzenedisulphonic acid by heating with an excess of sulphuric acid at 240° for about 12 hours with constant agitation. (3.) Production of sodium benzenedisulphonate by boiling the mass out with water, liming until neutral, filter-pressing, and treating the filtrate with sodium carbonate. The mixture is again filtered, and the effluent liquid evaporated to dryness. (4.) Fusing the dried salt with soda in an open cast-iron boiler fitted with agitators. (5.) Dissolving the heated mass in water, and adding hydrochloric acid to feebly acid reaction. (6.) Extracting the resorcinol from the acid solution with amyl alcohol in an extraction apparatus. (7.) Subjecting the extract to distillation to expel the alcohol; the residue containing the resorcinol being dried in enamelled iron pans. (8.) Purification of the resorcinol by fractional distillation in a vacuum. According to this method 125 kilos. of sodium benzenedisulphonate yield from 20 to 23 kilos. of pure resorcinol. D. B.

Constitution of Dinitroquinol and Formation of Nitranilic Acid. By R. Nietzki and J. Preusser (*Ber.*, **20**, 797—799).—The authors find that the diacetyldiamidoquinone, $C_6H_2O_2(NHAc)_2$, lately described by them (Abstr., 1886, 1024), is identical with the compound obtained by Bamberger (Abstr., 1884, 309) by the oxidation of triacetyltriamidophenol, to which he gave the formula $C_{20}H_{20}N_4O_8$. The simpler formula is undoubtedly the correct one, as when reduced with stannous chloride and hydrochloric acid the acetyl-groups are eliminated and diamidoquinol is formed. The compound liquefies at 265—270° without showing a definite melting point. The formation of quinol proves that the quinone-oxygens must as usual be in the para-position to one another, and the formation from triacetyltriamidophenol (prepared from picric acid), that the two amido-groups (and consequently the corresponding nitro-groups in the parent dinitroquinol) are both in ortho-positions to one of the oxygen-atoms or hydroxyl-groups respectively.

Nietzki has shown that this dinitroquinol is easily converted by nitric acid into nitranilic acid in which the two nitro-groups are in the para-position to each other. This and also the formation of paradinitrodihydroxyquinone from the same quinol, leave little doubt of the intermediate formation of a tetranitroquinol. L. T. T.

Action of Sodium Alkoxides on Benzaldehyde. By L. Claisen (*Ber.*, **20**, 646—650).—When 12 grams of sodium and 150 grams of methyl alcohol are heated on a water-bath and treated with 106 grams of benzaldehyde, the whole soon solidifies to a mass of

white crystals. The product consists of benzoic acid (56 grams) and benzyl alcohol (45 grams). If the mixture, after being heated for some hours on a water-bath, is first treated with glacial acetic acid (30 grams) and then with water, the product contains only a trace of benzoic acid, and consists chiefly of benzyl benzoate boiling at 323—324°. This boiling point was confirmed by preparing the salt by another method. Methyl benzoate and benzyl alcohol are also formed.

When benzyl benzoate and sodium methoxide are heated on a water-bath, a mixture of benzyl alcohol and methyl benzoate are formed; the same products are obtained when methyl benzoate and a solution of sodium in benzyl alcohol are warmed together.

Benzyl benzoate is also obtained by dissolving 1·5 gram of sodium in benzyl alcohol, adding 200 grams of benzaldehyde and heating for some days on a water-bath. 10 grams of glacial acetic acid and then water are added, and the oil distilled. The yield of benzyl benzoate is 150 grams. N. H. M.

Quinonedioxime and Dinitrosobenzene. By R. Nietzki and F. Kehrmann (*Ber.*, **20**, 613—616).—*Quinonedioxime*, $C_6H_4(NOH)_2$ [1 : 4], is obtained when 2 parts of hydroxylamine hydrochloride and $\frac{1}{2}$ part of hydrochloric acid are added to 1 part of quinol dissolved in the least possible quantity of cold water, and the whole allowed to remain for 12 hours. It crystallises in slender, colourless needles, decomposes at 240°, and is soluble in ether and hot water; the aqueous solution, however, undergoes partial decomposition. With dilute ammonia, it gives a greenish-yellow solution from which hydrochloric acid effects only a partial precipitation, the resulting solution yielding nitrosophenol when shaken with ether. When reduced with stannous chloride and hydrochloric acid, paraphenylenediamine is obtained.

Paradinitrosobenzene is formed by the oxidation of quinonedioxime in alkaline solution with potassium ferricyanide. It is a golden-yellow powder, insoluble in all neutral solvents, sublimes partially without decomposition, and is slightly volatile with steam. When boiled with a solution of hydroxylamine hydrochloride, it is reconverted into quinonedioxime. W. P. W.

Introduction of Acid Radicles into Ketones. By L. Claisen (*Ber.*, **20**, 655—657).—Benzoylacetophenone is obtained by mixing sodium ethoxide (free from alcohol) with ethyl benzoate and acetophenone; the whole solidifies with development of heat to a crystalline mass. This is washed several times with water, then with dilute soda solution, and is then treated with carbonic anhydride. The yield is 50 per cent. of the acetophenone employed. In a similar manner, ethyl benzoylacetate can be prepared from acetophenone and ethyl carbonate, but the yield is less satisfactory than in the case of benzoylacetophenone.

Nitrosoacetophenone, CHBz : N·OH, is readily prepared by adding acetophenone and then amyl nitrite to a well cooled solution of sodium in 20 parts of alcohol, and keeping the whole in a well closed

vessel for 12 to 24 hours at a low temperature. The reddish-brown sodium salt is freed from the liquid portion of the product by suction, washed with ether, dissolved in water and treated with acetic acid. It crystallises in prisms melting at 126—127°; the solution in sulphuric acid acquires an intense yellowish-red colour when treated with phenol. It dissolves in solutions of alkalis and alkaline carbonates, and is precipitated from the solutions slowly and incompletely by carbonic anhydride. When heated alone or with sulphuric acid, it is decomposed into benzoic and hydrocyanic acids.

The condensation products of ketones with aldehydes (Claisen and Schmidt, *Ber.*, **14**, 1459) are readily prepared by means of sodium alkoxides. Benzalacetophenone is obtained by mixing 12 grams of acetophenone with 10·5 grams of benzaldehyde, adding 3 c.c. of a 20 per cent. sodium methoxide solution, and keeping the whole for some days at a winter temperature. The yield is 90 per cent. of the theoretical. N. H. M.

Separation of Ortho- and Para-toluidine. By A. Wülfing (*Dingl. polyt J.*, **263**, 260).—On treating a mixture of para- and ortho-toluidine with nitrous acid, the latter is first attacked and converted into an amidoazo-compound, after which the acid acts on the para-compound, forming a diazoamido-derivative. Hence by employing an amount of acid equivalent to the proportion of orthotoluidine, the para-compound remains unaltered. It is recommended to effect the conversion by treating toluidine hydrochloride with sodium nitrite. This process is of special utility in separating the paratoluidine contained in crude toluidine. D. B.

Manufacture of Dimethylaniline. By O. Mühlhäuser (*Dingl. polyt. J.*, **263**, 348—351).—For the production of methylaniline on a commercial scale, two processes are in vogue: (1) Treating aniline with common hydrochloric acid of 21° B. and methyl alcohol, and heating the mixture under pressure; (2) Allowing methyl alcohol to act on aniline sulphate under pressure. After the completion of the reaction, the mass is rendered alkaline with lime, and distilled with steam. The oily distillate is then treated with dried salt to remove the last traces of water. The methylaniline so obtained may be used for the preparation of "violets," whilst for the manufacture of methylene-blue and malachite-green from dimethylaniline, it is necessary to subject the oil to fractional distillation, collecting the portion which comes over between 200° and 205°. D. B.

Conversion of Phenols into Amines. By V. Merz and P. Müller (*Ber.*, **20**, 544—550).—Continuing their experiments (this vol., p. 243), the authors have examined the action of mixtures of ammonium zinc bromide and ammonium bromide, and of ammonium zinc chloride and ammonium chloride on the three isomeric cresols when heated in sealed tubes for 40 hours at temperatures varying between 300° and 340°. The results are given in quantitative form, and show that under these conditions orthocresol yields about 10 per cent. of orthotoluidine and 50 per cent. of orthoditolylamine; meta-

cresol yields about 27 per cent. of metatoluidine and 50 per cent. of metaditolylamine; and paracresol yields from 25 to 45 per cent. of paratoluidine and 40 to 30 per cent. of paraditolylamine; the remainder in each case consisting of unaltered cresol, and from 2 to 6 per cent. of carbonaceous residue.

The boiling point of paraditolylamine was found to be 320—321°.

W. P. W.

Condensation Products of Ethyleneaniline with Aldehydes. By F. Moos (*Ber.*, **20**, 732—734).—Hofmann's diethyleneaniline (diphenylpiperazine if named according to Merz and Mason's proposals, this vol., p. 498), $C_2H_4 : (NPh)_2 : C_2H_4$, is a very stable compound, and this stability is probably due to its hexatomic ring formation. The author has obtained analogous compounds of the general formula $C_2H_4 : (NPh)_2 : CHR$, containing a pentatomic ring, by the condensation of ethyleneaniline with aldehydes.

Benzaldehyde and ethyleneaniline when heated together unite, with separation of water, to form a compound, $C_2H_4 : (NPh)_2 : CHPh$, which crystallises in colourless needles, melts at 137°, and distils without decomposition. Cumaldehyde and ethyleneaniline, under like conditions, yield a compound, $C_{24}H_{26}N_2$, crystallising in long, white, silky needles, melting at 124—125°, and soluble in ether and absolute alcohol. Salicylaldehyde and ethyleneaniline give a compound crystallising in groups of white, silky needles. It melts at 116°, and is easily soluble in ether and absolute alcohol, less so in benzene. Anisaldehyde and ethyleneaniline form a compound crystallising in colourless prisms, soluble in benzene and alcohol; it melts at 164°, and has the composition $C_{22}H_{22}N_2O$. Isobutaldehyde and ethyleneaniline undergo a similar reaction, yielding a compound, $C_{18}H_{22}N_2$. This crystallises in large, colourless needles, melts at 95°, and is easily soluble in benzene and ether, sparingly so in water. Œnanthaldehyde and ethyleneaniline yield the compound $C_{21}H_{28}N_2$, which crystallises in glistening needles, melts at 79°, and is easily soluble in ether, but sparingly so in benzene.

All these compounds, when warmed with dilute hydrochloric or sulphuric acid, are very readily reconverted into their constituents, thus differing from diphenylpiperazine. The author is now investigating the analogous compounds (containing a hexatomic ring) formed by the condensation of aldehydes with trimethyleneaniline.

L. T. T.

Action of Carbonyl Chloride on Ethylene- and Trimethylene-diphenyldiamine. By A. Hanssen (*Ber.*, **20**, 781—785).—*Trimethylenediphenyldiamine*, $C_3H_6(NHPh)_2$, was prepared by heating a mixture of aniline (4 mols.) and trimethylene bromide (1 mol.) on the water-bath. It is an oil which boils with decomposition above 360°. Its *sulphate* crystallises in minute needles melting at 155—156°, and is soluble in alcohol. With sodium nitrite the sulphate yields the corresponding *dinitrosamine* crystallising in greenish scales melting at 87°. When a solution of the diamine in benzene was slowly added to a well-cooled solution of carbonyl chloride in benzene, *trimethylenediphenylcarbamide*, $CO<^{NPh\cdot CH_2}_{NPh\cdot CH_2}>CH_2$, and *tri-*

methylenedicarbanilic chloride, $C_3H_6(NPh\cdot COCl)_2$, were formed. The former crystallises in silky scales which are soluble in alcohol and melt at 156° (uncorr.). The chloride crystallises in brittle needles, sparingly soluble in alcohol and melting at 102° (uncorr.). An alcoholic solution of the chloride, when treated with sodium, yielded *ethyl trimethylenecarbanilate*, which forms crystals melting at 56°. When heated with aniline in solution in benzene, the chloride yields the corresponding *anilide* which forms hard, transparent crystals melting at 153° (uncorr.).

Ethylenediphenyldiamine yields with carbonyl chloride under the above conditions, *ethylenediphenylcarbamide* and *ethylenedicarbanilic chloride*. The carbamide crystallises in scales, sparingly soluble in benzene, and melting at 206° (uncorr.). The chloride forms glistening prisms, soluble in benzene, and melting at 183° (uncorr.). The corresponding *ethyl salt* crystallises from alcohol in needles melting at 87—88°. The chloride is more stable than that described above, and the anilide, which appears to melt at about 170°, could not be obtained pure, but always contained undecomposed chloride. Neither of these chlorides is attacked by boiling alkalis or dilute acids. Their formation is analogous to that of the chloride obtained by Loeb (Abstr., 1885, 1213, and this vol., p. 42) by the action of carbonyl chloride on ethenyldiphenyldiamine.

When oxidised with chromic acid, ethylenediphenylcarbamide yielded diphenylparabanic acid. L. T. T.

The Tartrazines; a New Class of Dyes. By J. H. Ziegler and M. Locher (*Ber.*, **20**, 834—840).—Phenylhydrazine hydrochloride reacts with an equimolecular proportion of dihydroxytartaric acid to form *phenylizindihydroxytartaric* acid,

$$COOH\cdot C(N_2HPh)\cdot C(OH)_2\cdot COOH,$$

a yellow, crystalline precipitate. The compound melts at 218° with decomposition, is insoluble in cold, sparingly soluble in hot water, and soluble in concentrated sulphuric acid with brown coloration; it gives a brown precipitate with bleaching powder, and a red coloration with ferric chloride. It differs from dihydroxytartaric acid in its stability. Its *silver* salt forms orange-yellow leaflets, and the *barium* salt a golden precipitate. The *diphenylizindihydroxytartaric* acid formed from the above acid and phenylhydrazine hydrochloride, or directly from dihydroxytartaric acid, is an orange-yellow powder, sparingly soluble in water, soluble in alcohol. Its *ammonium* salt, $COONH_4\cdot C(N_2HPh)\cdot C(N_2HPh)\cdot COOH + H_2O$, crystallises in yellow leaflets, the *sodium* salt in red needles; the lead and aluminium salts are yellow precipitates, as also the silver imide. The acid, when heated with acetic anhydride, forms an anhydride crystallising in red needles, insoluble in alcohol. The *disulphonic* acid,

$$C_2(N_2H\cdot C_6H_4\cdot SO_3Na)_2(COOH)_2,$$

is best obtained from phenylhydrazinesulphonic acid, and sodium dihydroxytartrate in presence of soda; it is an orange-yellow powder, soluble in water, insoluble in alcohol. It has been introduced into

commerce under the name of "tartrazine" as a yellow dyestuff for wools; the diphenylizindihydroxytartaric acid, owing to its insolubility in acid baths, is of no practical application. V. H. V.

Condensation Products of Secondary Hydrazines with Dihydroxytartaric Acid. By J. H. Ziegler and M. Locher (*Ber.*, **20**, 841—844).—The secondary, like the primary hydrazines, react with dihydroxytartaric acid to form condensation products homologous with the tartrazines. Thus, from sodium dihydroxytartrate and diphenylhydrazine hydrochloride, in presence of hydrochloric acid, there are formed simultaneously a mono- and a di-condensation product. The former of these was not obtained in a fit state for analysis; the latter, $COOH{\cdot}C(N_2Ph_2){\cdot}C(N_2Ph_2){\cdot}COOH$, crystallises in the prismatic form, and is soluble in chloroform and acetic acid, insoluble in water; it melts at 177° with decomposition. The alkali salts are soluble in water; the copper salt is a green, and the lead and silver salts white precipitates. The acid dissolves in concentrated sulphuric acid with a red coloration, changing to green on standing. On fusion with phenol, it forms variously coloured dyes; with bromine, it yields a monobromo-derivative crystallising in leaflets. When heated with an excess of acetic anhydride, the acid yields an anhydride, $O(CO{\cdot}C{:}N_2Ph_2)_2$, crystallising in ruby-red prisms with greenish lustre. When heated, it forms a sintered mass at 200°, and melts completely at 222°; it dissolves in concentrated sulphuric acid with a green coloration. With ammonia, the anhydride forms a nitrogen compound, crystallising in rhombohedra which melt at 191—192°. This is probably an imide rather than an amide, from its insolubility in alkalis and alcohol, its low melting point, and the formation of a pyrroline-derivative when it is distilled with zinc-dust. V. H. V.

Preparation of Benzylrosanilinedisulphonic Acids. By A. Dahl (*Dingl. polyt. J.*, **263**, 393—394).—The production of mono-, di-, and tri-benzylrosanilines may be effected according to the laws generally applicable to the introduction of alkyl- into amido-groups, the entrance of the benzyl-groups being readily effected without the application of pressure. The benzylrosanilines formed are sparingly soluble in water, dissolve with a bluish-violet colour in benzyl chloride, and assume a greenish-blue colour on treatment in alcoholic solution with hydrochloric acid. The calcium salts form readily pulverisable masses having a metallic lustre. The salts of the alkalis and alkaline earths are readily soluble in water, and form lakes with the heavy metallic oxides, especially lead oxide and the oxides of tin. The calcium salt of the mono-acid imparts a ruby-coloured shade to wool dyed in an acid bath; the corresponding derivative of the di-acid gives a bluish-red colour, and the calcium salt of tribenzylrosanilinedisulphonic acid yields a reddish-violet shade. D. B.

Manufacture of Benzaldehyde-greens. By O. Mühlhäuser (*Dingl. polyt. J.*, **263**, 249—254; and 295—303).—1. Preparation of "Acid-green."—The formation of the leuco-base is effected by the condensation of 1 mol. of benzaldehyde and 2 mols. of ethylbenzyl-

aniline with anhydrous oxalic acid. On treating the resultant leuco-base with fuming sulphuric acid, a mixture of di- and tri-sulphonic acids of diethyldibenzyltriphenylmethane is obtained. On oxidation with lead dioxide, this yields the green acid dye, which is then converted into the sodium-derivative. 2. Preparation of "Malachite-green."—This comprises the following operations :—(*a.*) Formation of the pure, dry leuco-base by heating a mixture of dimethylaniline and benzaldehyde with zinc chloride. (*b.*) Oxidation of the base with lead dioxide and production of the green dye in a solid form, by treating the oxidised mass with zinc chloride and salting out the resultant double salt. (*c.*) Purification of the zinc salt by extraction with hot water and formation of the green base by the addition of ammonia to the aqueous extract. (*d.*) Production of the green crystals by redissolving the base in oxalic acid and reprecipitating with ammonia. 3. Preparation of "Brilliant green."—The leuco-base is obtained by heating a mixture of diethylaniline and benzaldehyde with dry oxalic acid. The product is dissolved in hydrochloric acid, treated with acetic acid, and oxidised with lead dioxide. The process used for the production of the green base and its purification is similar to the method adopted in the case of malachite-green; whilst the crystallisation is effected by dissolving the purified mass in sulphuric acid and adding ammonia. D. B.

Opiaurin. By C. Liebermann and P. Seidler (*Ber.*, **20**, 873—874).—Opianic acid and phenol, when heated with concentrated sulphuric acid, yield a cherry-red dye, the aldehydic group reacting with the phenol to form a leucaurin, $COOH{\cdot}C_6H_2(OMe)_2{\cdot}CH(C_6H_4{\cdot}OH)_2$, the latter being oxidised in the course of the process to an aurin, $C_{22}H_{18}O_6$, which it is proposed to call *opiaurin*. This compound was only obtained in an amorphous condition. It dissolves in alcohol and ether, and is insoluble in benzene and petroleum. It dissolves in alkalis with a purple-red coloration, becoming yellowish-brown when the solution is boiled, but returning, when cool, to its original tint. Similar dyes were obtained with other phenols, and the reaction can be used to detect opianic acid, as also to indicate the presence of an aldehydic group in an aromatic derivative. V. H. V.

Action of Aldehydes on Ammonium Thiocyanate. By L. Brodsky (*Monatsh. Chem.*, **8**, 27—40).—When a mixture of benzaldehyde and dry powdered ammonium thiocyanate is heated between 165° and 137° for some time, *benzylidenethiobiuret*, $C_9H_9N_3S_2$, is formed. When crystallised from alcohol, it forms microscopic prisms, and melts at 237° with partial decomposition. It is quite insoluble in water, slightly soluble in cold alcohol and ether, and more so in boiling alcohol. It dissolves in dilute alkalis, and is precipitated unchanged by acids; concentrated alkalis decompose it; concentrated sulphuric acid dissolves it, and it separates unaltered on dilution with water; nitric acid decomposes it in the cold. When an alcoholic solution is treated with solutions of the salts of heavy metals, salts are thrown down; the *silver* and *lead* salts are white, amorphous powders. When boiled with excess of acetic anhydride, an *acetyl* compound is

formed, having the composition $C_9H_7N_3S_2Ac_2$; it forms very brilliant, yellow, microscopic crystals melting at 189°.

When heated with excess of barium hydroxide solution on a water-bath, benzylidenethiobiuret is split up into benzaldehyde, barium thiocyanate, and thiocarbamide; there are also formed in small quantities, hydrogen sulphide, ammonia, and carbonic anhydride. From the above decompositions, the author concludes that the constitution of the substance is

$$HN<\begin{matrix}C(HS):N\\C(HS):N\end{matrix}>CHPh.$$

When cinnamaldehyde is heated with ammonium thiocyanate, two substances are formed, both of which are free from nitrogen.

Isovaleraldehyde and œnanthaldehyde, treated in the same way, give dark-red, viscous liquids, easily soluble in alcohol, ether, and acetic anhydride, and remaining unchanged on evaporation of the solvent. G. H. M.

Additive Products of Aromatic Thiocarbimides. By O. Helmers (*Ber.*, **20**, 786—791).—Whilst preparing isocyanic chlorides by Sell and Zierold's process (this Journal, 1875, 271), by passing a current of chlorine through solutions of thiocarbimides in chloroform, the author observed the formation of a crystalline precipitate, which, on continued passage of the chlorine, disappeared. If the passage of the chlorine through a chloroform solution of phenylthiocarbimide is stopped as soon as the solution becomes of a pale-yellow colour, a voluminous white precipitate gradually forms. The mother-liquor by further passage of chlorine yields a further crop of the substance. The compound contains chlorine, is very unstable, gives off hydrogen chloride when exposed to the air, and melts with decomposition at 150—160°. Attempts to obtain it in a pure state proved fruitless, but from its reactions there is little doubt that its formula is $(CS:NPh)_2Cl_2$. When dissolved in warm, dilute alcohol or digested with water at 100°, it yields *phenylthiocarbimide oxide*, $(CS:NPh)_2O$, hydrogen chloride being at the same time formed. The oxide crystallises in yellow needles melting at 118°. With paratolylcarbimide, similar compounds were formed, the *oxide*, $(CS:NC_7H_7)_2O$, crystallising in long needles melting at 139°. These oxides are analogous to those obtained by Sell in a similar way from fatty thiocarbimides (this Jour., 1873, 881). When the chlorides are treated with hydrogen sulphide, the decomposition proceeds further, symmetrical diphenylthiocarbamide, $CS(NHPh)_2$, being formed, probably according to the equation—

$$(CS:NPh)_2Cl_2 + 2H_2S = 2HCl + CS_2 + S + CS(NHPh)_2.$$

When bromine is substituted for chlorine in the above reaction, a red crystalline, unstable compound, $(CS:NPh)Br_2$, or $(CS:NPh)_2Br_4$, is formed, which, on exposure to air, gradually loses bromine, yielding the compound $(CS:NPh)_2Br_2$; this crystallises in glistening scales, and is more stable than the corresponding chloride. It melts with decomposition at 190°. The corresponding paratolyl-deri-

vative, $(CS:NC_7H_7)_2Br_2$, yields glistening scales melting at 210°. With alcohol or water, both compounds yield the corresponding oxides.

Proskauer and Sell state (this Jour., 1877, i, 67) that by the action of bromine on a chloroform solution of phenylthiocarbimide, they obtained a compound, $(CS:NPh)_2SBr_2$, which, when acted on by alcohol or glacial acetic acid, yielded the sulphide $(CS:NPh)_2S$. The author is, however, quite unable to corroborate this statement, as even when closely following out Proskauer and Sell's directions, he only obtained the compounds described above. L. T. T.

Manganese Benzoate. By K. Seubert (*Ber.*, **20**, 791—792).—Manganese benzoate is described in text-books as crystallising in clear, stable needles of the formula $Mn(C_7H_5O_2)_2,H_2O$, soluble in 20 parts cold water, more easily soluble in boiling water. This description dates from the researches of John made in the early part of this century. The author finds that from a solution of equal molecular proportions of sodium benzoate and manganese sulphate, the salt $Mn(C_7H_5O_2)_2,4H_2O$ crystallises in flat, rose-coloured, pliant prisms. They cleave readily in the direction of their most fully developed face, and the plates so obtained are optically biaxial. The crystals are tolerably stable, but gradually lose water, becoming opaque and white; in like manner, they lose water when heated with alcohol or water. An aqueous solution, if evaporated on the water-bath, yields a crystalline mass of the constitution and properties described by John. The solution saturated at 16° contains in 100 parts 6·556 parts of the tetrahydated or 5·5 parts of the monohydrated salt, a result corresponding with John's statement. L. T. T.

Isomerism in the Cinnamic Acid Series. By A. Michael and G. M. Browne (*Ber.*, **20**, 550—556).—Determinations of the vapour-density of the ethyl salts of the three bromocinnamic acids (Abstr., 1886, 702) show that the molecular weight is 255 in each case. The authors find that in the preparation of β-bromocinnamic acid (m. p. 158·5°) from phenylpropiolic acid by the action of hydrobromic acid a fourth bromocinnamic acid is formed, and can be separated by aid of the sparing solubility of its barium salt. The acid thus obtained exhibits a great similarity to the α-acid, as shown in the following table, but the authors consider them to be distinct:—

	α-Acid.	New acid.
Melting point.....	130—131°.	133—134°.
Crystalline form....	Long needles from water and chloroform.	Long needles exhibiting end faces from water; thick rhombic prisms from chloroform.
Solubility	Readily soluble in alcohol.	Readily soluble in alcohol and hot benzene, sparingly soluble in carbon bisulphide, hot water, and light petroleum.
Ammonium salt....	Flat needles sparingly soluble in cold water.	Flat needles, sparingly soluble in cold, easily soluble in hot water.
Barium salt	Lustrous, rhombic scales, anhydrous; solubility, 1·2 in 1000 of water at 6°.	Lustrous, rhombic scales, anhydrous; solubility 7·76 in 1000 of water at 6°.

The concluding portion of the paper is devoted to a criticism of the hypothesis put forward by Erlenmeyer to explain the isomerism of the bromocinnamic acids (Abstr., 1886, 945), which is rejected by the authors in favour of their theory of alloisomerism (*ibid.*, 687).

W. P. W.

Derivatives of Phenylmethacrylic Acid and of Phenyliso-butyric Acid. By L. Edeleano (*Ber.*, **20**, 616—622).—The author finds that the yields of phenylmethacrylic acid prepared by Conrad and Bischof's method (*Annalen*, **204**, 188) is only slightly lessened if, instead of using sealed tubes, the materials are heated at 125—130° for 30 hours in a flask with a cooling tube attached. *Phenylmeth-acrylamide*, $CHPh:CMe\cdot CONH_2$, crystallises in prismatic scales, melts at 128°, and is sparingly soluble in ether and cold alcohol, soluble in hot water.

Phenylisobutyramide crystallises in needles, melts at 109°, and is readily soluble in alcohol and ether, soluble in hot water. When treated with bromine and aqueous potash, it is converted into *phenyl-isopropylamine*, $CH_2Ph\cdot CMeH\cdot NH_2$, a colourless, strongly refractive liquid boiling at 203°; its platinochloride crystallises in matted needles, and is sparingly soluble in water.

Methyl phenylmethacrylate is obtained when phenylmethacrylic acid is dissolved in an equal weight of methyl alcohol and the solution saturated with hydrogen chloride. It crystallises in long needles, melts at 39°, boils at 254°, and is soluble in all ordinary solvents. Two nitro-derivatives are formed when the methyl salt is treated with five times its weight of fuming nitric acid (sp. gr. = 1·52), and can be separated by crystallisation from alcohol. The less soluble compound is *methyl paranitrophenylmethylacrylate;* it crystallises in rectangular scales, and melts at 115°. *Paranitrophenylmethacrylic acid,*

$$NO_2C_6H_4\cdot CH:CMe\cdot COOH,$$

crystallises in rhombs, melts at 208°, and is soluble in hot alcohol and acetic acid, very sparingly soluble in all ordinary solvents in the cold. Its *silver* salt, $C_{10}H_9NO_2Ag$, crystallises in slender, white needles and is soluble in hot water. The more soluble compound is obtained by evaporation of the alcohol as a liquid, which solidifies in a freezing mixture and yields *orthonitrophenylmethacrylic acid* when saponified. This is a feebly coloured powder, melts at 164—165°, and is readily soluble in alcohol and ether, sparingly soluble in benzene and light petroleum.

When phenylmethacrylic acid is nitrated, *dinitrophenylpropylene*, $C_6H_3(NO_2)_2\cdot CH:CHMe$, is obtained together with other nitration products. It crystallises in pale-yellow needles, melts at 118°, and is soluble in alcohol.

W. P. W.

Preparation of Ethyl Benzoylacetate. By L. Claisen and O. Lowman (*Ber.*, **20**, 651—654).—Ethyl benzoylacetate is prepared by heating 140 grams of sodium methoxide with 300 grams of ethyl benzoate in a water-bath until the mixture becomes solid. It is then mixed with 350 grams of ethyl acetate and heated for 15 hours on a water-bath in a reflux apparatus; 150 grams of glacial acetic acid are

added, and then water; the oil thus separated is washed with aqueous soda, dried over potash, and distilled in a partial vacuum (20 mm.). The yield of pure salt is 33 per cent. of the weight of ethyl benzoate. Ethyl acetoacetate, unchanged ethyl benzoate, and dihydrobenzoylacetic acid are also obtained. Almost the same yield is obtained when the reaction is allowed to take place at the ordinary temperature.

The authors think it probable that in the formation of ethyl acetoacetate and benzoylacetate, the compounds $CMe(OEt)_2{\cdot}ONa$ and $CPh(OEt)_2{\cdot}ONa$ respectively are first formed and that these then react with ethyl acetate, yielding the acetoacetate or benzoylacetate and 2 mols. of ethyl alcohol. N. H. M.

Oak-tannin. By C. Böttinger (*Ber.*, **20**, 761—766).—This was obtained by treating the syrupy commercial "oakwood-extract" with about 20 times its volume of water, filtering off the insoluble substance, evaporating the solution to dryness, and treating the powdered residue with acetic anhydride. The tannin was thereby converted into an acetyl-compound which was soluble in excess of the anhydride. When the acetic solution is poured into water, the acetyl-derivative $C_{15}H_7Ac_5O_9$ is precipitated as a heavy greyish-white powder. When exposed to the air, it gradually loses its acetyl as acetic acid. The acetyl-compound is soluble in ethyl acetate, chloroform, glacial acetic acid, ethyl acetoacetate, &c., insoluble in water and cold alcohol. Boiling alcohol eliminates the acetyl-groups and then dissolves the tannin. Cold concentrated sulphuric acid acts like boiling alcohol. The free tannin is converted into an anhydride by inorganic acids. The anhydride, when heated with ethyl iodide and alcoholic potash, yields an ethyl salt which decomposes when heated. The best means of obtaining the free tannin from the aceto-derivative is to heat the latter with water at 135° in closed tubes. The tannin thus obtained when dried in the desiccator has the composition $C_{15}H_{12}O_9 + 2H_2O$. It loses I mol. H_2O at 100° and the second at 135°. The author has obtained from the aceto-compound two bromo-derivatives, $C_{15}H_{10}BrAcO_9$ and $C_{15}H_7Br_4AcO_9$.

The author believes this oak-tannin to be a methyl salt of digallic acid. L. T. T.

Etherification of Opianic Acid. By C. Liebermann and S. Kleemann (*Ber.*, **20**, 881—882).—Opianic acid is characterised by its ready susceptibility to etherification; this property may be utilised for its purification, as the ethereal salts formed are decomposed when boiled with water. The methyl salt melts at 102°, the ethyl salt at 92°, and the propyl salt at 103°. Possibly the above property is dependent on the constitution of opianic acid as an ortho-aldehydic acid. V. H. V.

Reduction of Nitro-opianic Acid. By S. Kleemann (*Ber.*, **20** 875—881).—Nitro-opianic acid, when treated with concentrated sodium methoxide, is converted into a *nitroso*-acid, crystallising in long, golden-green needles which melt at 175—176° and decompose

at 200°. It is sparingly soluble in water, more readily in alcohol, and is distinguished from the nitro-acid in that it does not react with phenylhydrazine under the same conditions. Its *silver* salt crystallises in colourless needles, sparingly soluble in cold, readily in hot water. When reduced with stannous chloride, the nitroso- is converted into an *amido*-acid, which is crystalline, but owing to decomposition is not of definite melting point; its solution gives a green coloration with ferric chloride. Its hydrochloride, when heated with acetic anhydride and sodium acetate, yields a compound, $C_{24}H_{24}N_2O_{11}$, derived from the condensation of 1 mol. of the amido-acid and 1 of the anhydride with elimination of 1 mol. of water. It forms ill-defined crystals, insoluble in water, sparingly soluble in alcohol, and melts at 232—233° with decomposition. On reduction with zinc-dust and ammonia, the nitroso-acid yields an *azo*-acid,

$$COOH\cdot C_6H(OMe)_2<\begin{matrix}CH_2\cdot O\cdot CH_2\\ N\!=\!=\!=\!=\!N\end{matrix}>C_6H(OMe)_2\cdot COOH,$$

not obtainable in a definite crystalline form; it melts with decomposition at 245°, and dissolves in alkalis with a yellow, and in concentrated sulphuric acid with a purple coloration. Its *silver* salt is a yellowish-brown, flocculent precipitate: its *ethyl* salt crystallises in small, yellow needles melting at 101°, insoluble in water, soluble in alcohol and benzene.

Meconineacetic acid (this vol., p. 47) dissolves in ammonia to form a yellow liquid, which is decolorised when boiled with zinc-dust. The acid is insoluble in water, but dissolves in alcohol with partial decomposition. V. H. V.

ψ-Meconine. By O. Salomon (*Ber.*, **20**, 883—889).—As it is to be supposed that meconine stands to hemipinimide in a relation analogous to that of phthalide to phthalimide, it should be possible to convert hemipinimide into the former, but experiments showed that instead of meconine, a compound isomeric with it, called provisionally ψ-meconine, is produced.

On hydrogenation with tin and hydrochloric acid, hemipinimide yields *hemipinimidine*, $C_{10}H_{11}O_3N$, analogous to phthalimidine; this crystallises in leaflets melting at 181°, soluble in benzene. With nitrous acid, it yields a nitroso-derivative, $C_{10}H_{10}NO_3\cdot NO$, crystallising in silky needles which melt at 156° with decomposition, sparingly soluble in cold, more readily in hot water. On treatment with dilute soda, this compound yields *ψ-meconine* or dimethoxyphthalide, $C_6H_2(OMe)_2<\begin{matrix}CH_2\\ CO\end{matrix}>O$ [OMe : CH_2 : CO : OMe = 1 : 2 : 3 : 6], a formula which may explain the isomerism of this compound with meconine, which contains the CH_2 and CO groupings in the reverse positions. ψ-Meconine crystallises in long, colourless needles which melt at 123—124°, soluble in benzene, alcohol, and ether. With fuming nitric acid, it yields a nitro-derivative, $C_{10}H_9O_4NO_2$, crystallising in yellow needles which melt at 166°; on further treatment with nitric acid, oxalic acid is produced. On reduction, an amido-derivative is formed, a yellowish substance melting at 165°, and distinguished

from amido-meconine (m.p. 171°) by its melting point, the difference in solubility in benzene, and the more marked basic properties of the former. *Bromo-ψ-meconine* is a white flocculent precipitate, which melts at 141—142°, and is soluble in benzene, insoluble in petroleum.

The isomeric meconines are also distinguished by their behaviour towards oxydising agents; thus with manganese dioxide and sulphuric acid meconine yields opianic acid almost in quantitative proportions, whilst ψ-meconine is, for the most part, unaltered. With nitric acid (sp. gr.= 1·14), ψ-meconine yields, besides the nitro-derivative, nitrohemipinic acid; but meconine, under the same conditions, yields nitromeconine. It is further shown that hemipinic anhydride when hydrogenised yields ψ-meconine. V. H. V.

Action of Potassium Cyanide on Meconine. By W. Bowman (*Ber.*, **20**, 890—891).—Another method of distinguishing the two isomeric meconines described in the preceding Abstract is their behaviour with potassium cyanide; ψ-meconine remains unaltered while meconine is converted into normethylmeconine, first isolated by Matthiessen and Foster. The change is probably to be explained by the alkaline nature of the potassium cyanide which, at the high temperature, effects the removal of the methyl-group. V. H. V.

Orthotolylphthalimide. By M. Kuhara (*Amer. Chem. J.*, **9**, 51—58; comp. Abstr., 1881, 1039).—According to v. Gerichten, phthalyl chloride is either $C_6H_4<\overset{CCl_2}{CO-}>O$ or a mixture of this substance with the normal chloride. By treating phthalyl chloride with ammonia, a substance isomeric with phthalimide was on one occasion obtained, but its preparation could not be repeated (*loc. cit.*). By substituting orthotoluidine, a similar result is obtained, only one substance being produced, and hence it is probable that phthalyl chloride is not a mixture of two substances. The substance produced is—

Orthotolylphthalimide, $C_6H_4:(CO)_2:N\cdot C_6H_4Me$, melting at 182°, and identical with Froelich's phthalorthotoluide, obtained from phthalic anhydride and orthotoluidine.

Orthotolylphthalamic acid, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4Me$, is obtained by boiling the imide with ammonia, and acidifying; it crystallises in needles. The two lead salts and silver salts, as well as the normal barium salt, are described.

Methyl-derivatives of Orthotolylphthalamic Acid.—The above acid was treated with sodium in presence of xylene and then with methyl iodide, and finally with water in the presence of the excess of sodium used; the methylated compound was thus saponified, and yielded phthalic acid and dimethylorthotoluidine, which is formed most probably from the decomposition of the methiodide of sodium methylorthotolylphthalamate, $COONa\cdot C_6H_4\cdot CO\cdot NMe_2(C_7H_7)I$. Neither this compound nor sodium methylorthotolylphthalamate,

$$COONa\cdot C_6H_4\cdot CO\cdot NMe\cdot C_7H_7,$$

could be properly purified, as they do not crystallise readily.

The existence of the salts described is held to be in favour of the symmetrical formula for phthalyl chloride. H. B.

Syntheses of the Ethyl Salts of Ketonic Acids. By W. Wislicenus (*Ber.*, **20**, 589—595).—An almost theoretical yield of ethyl oxalacetate (this vol., p. 234) can be obtained by employing twice the weight of sodium indicated by theory, inasmuch as one-half of the metal enters into combination to form sodium ethoxide. When ethyl acetate (2 mols.) is slowly added to a solution of ethyl oxalate (1 mol.) in ether to which sodium wire (4 atoms) has been added, and the well-cooled product is treated with water, the aqueous layer yields ethyl ketipate (this vol., p. 362) on acidification.

Ethyl phenyloxalacetate, COOEt·CHPh·CO·COOEt, is prepared by dissolving 10 grams of ethyl oxalate in 40 grams of ether, adding 3·2 grams of sodium wire, and then gradually adding 12 grams of ethyl phenylacetate; the product is decomposed by dilute sulphuric acid, and the compound extracted from the ethereal layer by means of aqueous soda. It is a very viscous oil, decomposes on distillation, is insoluble in water, readily soluble in alkalis, ether, and alcohol. The alcoholic solution gives an intense red coloration with ferric chloride. When boiled with 10 per cent. sulphuric acid, it decomposes with evolution of carbonic anhydride and formation of phenylpyruvic acid.

Phenylpyruvic acid, $CH_2Ph·CO·COOH$, crystallises in lustrous scales, melts at 153° with a feeble evolution of gas, and is readily soluble in ether and alcohol, soluble in hot chloroform and benzene, sparingly soluble in hot water, and insoluble in cold water and light petroleum. The alcoholic solution gives a dark-green coloration with ferric chloride. The *phenylhydrazide* crystallises in small, yellowish needles, melts at 160—161° with evolution of gas, and is insoluble in water and light petroleum, sparingly soluble in ether, soluble in alcohol, chloroform, and benzene. It is probably identical with the phenylhydrazide of Plöchl's phenylglycidic acid (this vol., p. 142).

Ethyl phthalate is not attacked by sodium at 100°, but when ethyl acetate is gradually added a reaction occurs, resulting in the formation of an acid of the composition $C_9H_6O_2$. This crystallises in small, lustrous, yellow needles, melts at 130—132°, and is soluble in alcohol, ether, and benzene. Its salts have generally an intense yellow coloration, the *iron* salt is dark-red. When treated with nitrous acid, it yields a yellow nitroso-derivative; the *phenylhydrazide*, $C_9H_6O(N_2HPh)$, crystallises in microscopic needles, melts at 162—163° with decomposition, and is readily soluble in alcohol, ether, and benzene. When the acid is boiled with water, an acid of the composition $C_{18}H_{10}O_3$ is obtained in microscopic scales; this is insoluble in all solvents, melts at 206—208° with complete decomposition, and yields salts showing an intense coloration; thus the salts of the alkaline metals are intensely violet, the *silver* salt is dark-red, the *zinc* salt intensely violet-blue, and the *copper* salt deep-blue. W. P. W.

Synthesis of Ethyl Trimesate. By A. Piutti (*Ber.*, **20**, 537—539).—Ethyl sodacetate does not react with formic acid either in the cold or on heating, and when treated with ethyl formate yields only sodium ethoxide, carbonic oxide, and ethyl acetoacetate. If, however, a mixture of ethyl acetate and ethyl formate in equimolecular pro-

portions is treated with sodium, hydrogen and carbonic oxide are evolved and ethyl trimesate is obtained. The yield amounts to 6 to 7 per cent. on the ethyl formate used; at the same time ethyl acetoacetate is also formed in some quantity. When mixtures in equimolecular proportions of methyl formate and ethyl acetate, and of ethyl formate and methyl acetate are respectively treated with sodium, a mixture of ethyl and methyl trimesate is obtained in both cases; this melts at 105—110° after one crystallisation from alcohol.

Methyl trimesate crystallises in small, silky needles melting at 143°, and a mixture of it and ethyl trimesate in equal proportions melts at 105—110°. W. P. W.

Rosindole. By E. Fischer and P. Wagner (*Ber.*, **20**, 815—818).—Methylketole when heated with benzoic chloride in presence of zinc chloride yields, in addition to a benzoyl-derivative, the hydrochloride of a base, $C_{25}H_{20}N_2$. This salt, which may be completely separated from its aqueous solution by the addition of sodium chloride, forms green iridescent crystals, resembling in appearance rosaniline hydrochloride; on adding an alkali, the free base is obtained in reddish-yellow, prismatic crystals, which change colour at 250° and fuse completely at 270°. With acids, it forms salts which are soluble in water and alcohol, and dye silks and wools of a red colour; it appears also to form unstable salts with alkalis, readily decomposed by water. When the alcoholic solution of the base is treated with zinc-dust and ammonia, it is decolorised with formation of benzylidenemethylketole, a change analogous to the formation of leucaniline from rosaniline. From the similarity in colour, dyeing properties, and chemical reactions of the above base with those of rosaniline, it is proposed to call it *dimethylrosindole;* it is probably the anhydride of a carbinol, $CPh(C_9H_6N)_2{\cdot}OH$.

Benzoylmethylketole crystallises in glistening leaflets, melting at 82°, and is moderately soluble in ether and alcohol, sparingly soluble in water. V. H. V.

Methylation of Indole-derivatives. By E. Fischer and A. Steche (*Ber.*, **20**, 818—820).—When methylketole is heated with methyl alcohol and iodide, it yields the hydriodide of a basic compound, $C_{11}H_{13}N$, crystallising in prisms, and from which the base itself is obtained as a colourless oil boiling at 243°. This compound is not an indole-derivative in that it gives neither the pine-wood reaction nor the red picrate; also it is unaltered by nitrous acid, and differs from the indoles by its strongly basic character. It is probably a dimethyldihydroquinoline, containing a methyl-group attached to the nitrogen, and another in the quinoline residue; but of this view no proof is given. Of its salts, the sulphate crystallises in leaflets soluble in alcohol, and the *picrate* in golden-yellow leaflets; the *hydrochloride* forms a compound with ferric chloride.

In like manner, dimethylindole yields a base, $C_{12}H_{15}N$, boiling at 244°, and dimethyl-β-naphthindole yields a compound, $C_{15}H_{15}N$, probably a methyldihydronaphthaquinoline, which crystallises in colourless leaflets, melts at 115°, and is readily soluble in mineral acids forming crystalline salts. V. H. V.

Derivatives of Diphenyl. By P. Adam (*Compt. rend.*, **104**, 691—693).—*Diphenyl-diphenyl ketone*, $CO(C_6H_4Ph)_2$, is obtained in almost theoretical quantity, when a mixture of diphenyl, 15 parts, carbon bisulphide, 20 parts, and carbonyl chloride, 10 parts, is added to 15 parts of aluminium chloride. There is an immediate evolution of hydrogen chloride, and towards the end of the reaction the flask is placed in tepid water. The carbon bisulphide is distilled off, and the residue washed with dilute alkali, then with pure water, dried, and recrystallised from boiling benzene or acetone. Diphenyl-diphenyl ketone forms white needles which melt at 229°, and are somewhat soluble in acetone, benzene, and chloroform, but almost insoluble in benzene and light petroleum. It is reduced with great difficulty. When dissolved in a mixture of alcohol and benzene, and treated with a large quantity of sodium amalgam, it yields diphenyl-benzhydrol, $CH(C_6H_4Ph)_2{\cdot}OH$, which crystallises readily, melts at 151°, and is very soluble in alcohol.

The action of carbonyl chloride on diphenyl in presence of aluminium chloride, with the aid of heat, but without carbon bisulphide, also produces the ketone, but the yield is smaller. The use of carbon bisulphide has advantages in the case of acid chlorides, but not with haloïd derivatives of hydrocarbons.

Acetic chloride acts readily on diphenyl in presence of aluminium chloride, whether carbon bisulphide is present or not. The product is diphenyl methyl ketone, or diphenylacetyl, $C_6H_4Ph{\cdot}COMe$; this forms white, flexible, nacreous crystals, readily soluble in alcohol or acetone; it melts at 121°, and boils at 325—327°. C. H. B.

Condensation of Diphenic and Orthodiphenylcarboxylic Acids. By C. Graebe and C. Aubin (*Ber.*, **20**, 845—848).—Anschütz has shown that diphenic acid yields an anhydride with acetic chloride or acetic anhydride, but Mensching and Graebe, by the action of concentrated sulphuric acid, obtained a substance of the same composition, but of higher (7°) melting point. In this paper, these experiments are repeated; in the latter case, *diphenyleneketonecarboxylic acid*, $<^{-CO-}_{C_6H_4}>C_6H_3{\cdot}COOH$, is produced, which crystallises in needles melting at 227°; its salts are also crystalline; the *ethyl* salt crystallises in needles melting at 103°, and the *methyl* salt at 132°. The acid combines with hydroxylamine to form a colourless acetoxime, and with phenylhydrazine it yields a condensation product. The potassium salt is reconverted into the salt of diphenic acid by fusion with alkali. On vaporisation, the acid is decomposed into carbonic anhydride and diphenylene ketone. In like manner, orthodiphenylcarboxylic acid is converted into diphenylene ketone by heating with concentrated sulphuric acid. The diphenic anhydride, isomeric with the above acid, crystallises in pyramidal needles melting at 217°, and sparingly soluble in alcohol and ether. When boiled with solutions of alkalis, it is converted into the potassium salt of diphenic acid.

V. H. V.

Formula of Diphenic Acid. By C. Graebe (*Ber.*, **20**, 848—850).—In this paper, the question is discussed whether the diphenic acid

$COOH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COOH$ [COOH : COOH = 1 : 1′] is isomeric or identical with the acid, [COOH : COOH = 1 : 6′]. If the two benzene nuclei were in the same plane, these two acids would be identical; but if they were situated in different planes, it is possible that the acids might be isomeric. At present, the evidence is insufficient to decide the question. V. H. V.

Preparation of β-Nitronaphthalene. By E. Lellmann (*Ber.*, **20**, 891—893).—The following method has been found to be the most practicable for the preparation of β-nitronaphthalene; the mixture of the ortho- and para-nitroacetonaphthalide is boiled with a 14 per cent. potash solution in presence of alcohol, and the mixture of the ortho-aceto-compound and para-nitronaphthalene is treated with ethyl nitrite, when the diazo-amido-derivative of para-nitronaphthylamine separates as a brown precipitate. This is filtered off, and the orthonitroacetonaphthalide crystallises out, and, after purification, is best decomposed by an alcoholic solution of hydrogen chloride. The orthonitronaphthylamine thus obtained serves for the preparation of the nitronaphthalene. V. H. V.

β-α-Azonaphthalene. By R. Nietzki and J. Göttig (*Ber.*, **20**, 612—613).—*β-α-Amidoazonaphthalene*, $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$, is prepared by diazotising β-naphthylamine (1 mol.), adding α-naphthylamine hydrochloride (1 mol.), and subsequently precipitating the base with soda; it crystallises in yellowish-brown needles, melts at 152°, and is soluble in alcohol. Its solution in concentrated sulphuric acid has a violet coloration.

β-α-Azonaphthalene, $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_7$, is obtained by adding 3 parts of sulphuric acid to a solution of 1 part of β-α-amidoazonaphthalene dissolved in 50 parts of alcohol, diazotising, boiling the whole for some time, and afterwards precipitating with water. It crystallises in dark-brown scales with steel-blue iridescence, melts at 136°, and is more soluble in alcohol, acetic acid, &c., than the corresponding α-α-derivative (Abstr., 1886, 245). It dissolves in sulphuric acid yielding a violet solution. W. P. W.

New Method of Preparing Azines. By O. N. Witt (*Ber.*, **20**, 571—577).—When diazobenzenesulphonic acid (1 mol.) is gradually added to phenyl-β-naphthylamine (1 mol.) dissolved in acetic acid at 50°, and the mixture afterwards treated with potassium carbonate, iridescent, blood-red needles of *sulphobenzeneazophenyl-β-naphthylamine*, $NHPh{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$ [N_2 : NHPh = 1 : 2], are obtained. These dissolve readily in water, and the solution, even when dilute, solidifies in the cold to a transparent, red jelly. Concentrated sulphuric acid produces a cherry-red colour; whilst stannous chloride in acid solution decolorises the compound with formation of phenylorthonaphthylenediamine. Sulphobenzeneazophenyl-β-naphthylamine is the lowest member of a series of beautiful, ponceau-red dyes, which have great tinctorial power, but are extremely sensitive to light; sunlight rapidly producing the same change that is brought about when the dyes are boiled with dilute mineral acids.

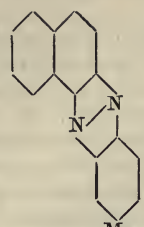
Naphthaphenazine, [1 : 2] $C_{10}H_6\langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle C_6H_4$ [1 : 2].—Sulphobenzene-azophenyl-β-naphthylamine, when boiled with dilute sulphuric acid, decomposes quantitatively into sulphuric acid and naphthaphenazine. This crystallises in lustrous, citron-yellow needles or prisms, melts at 142·5°, sublimes at about 200° in long, flat needles, and boils above 360° with slight decomposition. It is readily soluble in hot benzene, very sparingly in alcohol and ether, and dissolves in concentrated sulphuric acid with a brownish-red colour. With mineral acids, naphthaphenazine forms crystalline salts which are decomposed by water, and show a peculiar dimorphism. The two *sulphates* are respectively obtained in cinnabar-red tufts of needles or garnet-red, compact, twinned prisms; the *nitrates* are very sparingly soluble, one forms orange-yellow and the other brick-red aggregates of needles; the *hydrochloride* obtained by dissolving the azine in hydrochloric acid forms long, reddish-yellow needles, and when heated at 150° is converted into the second form, which crystallises in needles; the two forms of each salt are convertible into one another. Stannous chloride reduces the azine to the corresponding hydro-compound, crystallising in violet needles. Naphthaphenazine can also be obtained by the action of β-naphthaquinone (1 mol.) on orthophenylenediamine (1 mol.) in 50 per cent. acetic acid at 0°, and by oxidising a mixture of orthophenylenediamine and β-naphthol in equimolecular proportions with potassium ferricyanide in alkaline solution.

W. P. W.

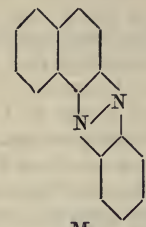
Constitution of the Isomeric Tolunaphthazines. By O. N. Witt (*Ber.*, **20**, 577—581).—Inasmuch as naphthaphenazine (comp. preceding Abstract) is a 1 : 2-derivative of naphthalene, the tolunaphthazine (m. p. = 179·8°) obtained by the simultaneous oxidation of β-naphthol and orthotoluylenediamine (Trans., 1886, 404), must have a similar constitution. Hinsberg's tolunaphthazine (m. p. = 139—142°), from its method of preparation (Abstr., 1885, 909), must also be a 1 : 2-derivative of naphthalene, and to assign to each its constitutional formula (in other words to determine the position of the methyl-group in the benzene nucleus) sulphobenzeneazoparatolyl-β-naphthylamine was prepared from paratolyl-β-naphthylamine and diazobenzenesulphonic acid, and afterwards decomposed by boiling with dilute sulphuric acid (comp. preceding Abstract). The *tolunaphthazine* so obtained, however, crystallises from benzene in needles and prisms, and from alcohol, in which it is very sparingly soluble, in lustrous, citron-yellow scales; it melts at 169°, and forms well-crystallised salts. The solution in sulphuric acid is dark cherry-red in colour, and the *sulphate* crystallises in long, orange-yellow, lustrous needles. The same tolunaphthazine can be prepared from "wool-black," a dye obtained by the action of diazobenzenedisulphonic acid on paratolyl-β-naphthylamine, by boiling it with dilute sulphuric acid.

The author finds that when equal weights of the tolunaphthazines melting at 169° and 179·8° respectively, are mixed and crystallised from alcohol, a compound melting at 139—142°, and undistinguishable

from Hinsberg's modification, is obtained. The following are the constitutional formulæ assigned to the isomeric tolunaphthazines :—



M. p. = 169°.



M. p. = 179·8°.

Paratolyl-β-naphthylamine, obtained by heating paratoluidine hydrochloride with β-naphthol for eight hours at 200°, crystallises in snow-white scales, melts at 104°, and is soluble in alcohol, benzene, ether and acetic acid, the solutions showing a beautiful violet-blue fluorescence. W. P. W.

Acenaphthene. By C. Graebe (*Ber.*, **20**, 657—659).—In oxidising acenaphthene to naphthalic acid, a *compound* of the formula $C_{24}H_{14}O_2$ is formed. The latter sublimes when heated (at 269°) in red needles which melt at 260°. It is sparingly soluble.

When acenaphthene, dissolved in glacial acetic acid, is oxidised with chromic acid, a compound is obtained which crystallises in reddish-yellow needles melting at 230°. Analyses of the compound, after prolonged treatment with sodium carbonate solution, point to the formula $C_{10}H_6<^{CO}_{CO}>$; when oxidised, it is converted into naphthalic acid. N. H. M.

Derivatives of Acenaphthene. By F. Quincke (*Ber.*, **20**, 609—611).—*Nitracenaphthene*, $C_{12}H_9{\cdot}NO_2$, is obtained when fuming nitric acid is added to a solution of acenaphthene in acetic acid. It crystallises in yellow, matted needles, melts at 102°, and is soluble in alcohol, ether, light petroleum, acetic acid, and hot water. When it is reduced with tin and hydrochloric acid *amidoacenaphthene*, $C_{12}H_9{\cdot}NH_2$, is formed. This is a white, asbestos-like compound, melts at 96°, is volatile with steam, and yields a crystalline hydrochloride. W. P. W.

Dimethylanthragallol. By W. Birukoff (*Ber.*, **20**, 870—873).—*Dimethylanthragallol*, $C_{14}H_3Me_2O_2(OH_2)$ [Me_2 : $(OH)_3$ = 1 : 3 : 1′ : 2′ : 3′], is obtained, in like manner to the trimethyl-derivative, by heating metaxylic and gallic acids with concentrated sulphuric acid; it crystallises in golden-red needles; it resembles anthragallol as regards its solubility in alkalis and its absorption-spectrum. On distillation over zinc-dust, it yields a dimethylanthracene, melting at about 220°, and yielding on oxidation a quinone crystallising in white needles melting at 112°. These compounds are isomeric, therefore, with those which Gresly obtained melting at 202° and 180° respectively. V. H. V.

Trimethylanthragallol. By H. Wende (*Ber.*, **20**, 867—870).—*Trimethylanthragallol*,

$$C_{14}H_2Me_3O_2(OH)_3\ [Me_3 : (OH)_3 = 1:3:4:1':2':3'],$$

is obtained by heating a mixture of 2 parts of gallic acid, 3 parts of durylic acid, and 30 parts of concentrated sulphuric acid. The crude product is finally exhausted with benzene, which dissolves the trimethylanthragallol, leaving the rufigallic acid. The former crystallises in glistening, brown needles, melting at 244°, soluble in alcohol, sparingly soluble in benzene; it dissolves in concentrated sulphuric acid with a violet-red coloration; it resembles anthragallol in its absorption-spectrum and dyeing properties. Its *triacetyl*-derivative, $C_{14}H_2Me_3O_2(OAc)_3$, crystallises in pale-yellow, rhombic tables, melting at 174°. Trimethylanthragallol, on distillation over zinc-dust, yields a solid trimethylanthracene, identical probably with that obtained by Gresly, together with a liquid hydrocarbon which, though not fully examined, is considered to be a dihydride of trimethylanthracene.

V. H. V.

Hydroxyanthraquinone Dyes. By C. Liebermann and W. Wense (*Ber.*, **20**, 862—866).—Liebermann and Kostanecki have shown that only those hydroxyanthraquinones which contain the hydroxyl-groups in the alizarin-position can be mordanted on fabrics. In order to confirm this view, a compound, at once an alizarin and a quinazin, has been prepared from hemipinic acid and quinol by heating a mixture of the two with concentrated sulphuric acid. There is thus formed a *dimethyl ether* of a *quinalizarin*, $C_{14}H_4(OMe)_2(OH)_2O_2$ $[(OMe)_2 : (OH)_2 = 1:2:1':4']$, which crystallises in brown-red minute leaflets, melting at 225—230°, soluble in alkalis with violet coloration and in concentrated sulphuric acid with a blue coloration. With mordants, it gives but a faint colour. Its acetyl-*derivative* crystallises in small needles melting at 210—211°, sparingly soluble in cold alcohol and acetone, but more readily in hot. *Quinalizarin*, $C_{14}H_4(OH)_4O_2$, obtained from the above by heating it with hydrochloric acid, crystallises in deep-red needles, exhibiting no signs of fusion at 275°. Its reactions with alkalis and with concentrated sulphuric acid are similar to those of the dimethyl ether; its *barium* and *calcium* salts are insoluble in water. It possesses strong dyeing powers, resembling those of alizarin. On distillation with zinc-dust at 210°, it yields anthracene. Its tetracetyl-derivative, $C_{13}H_4(OAc)_4O_2$, crystallises in needles melting at 201°, soluble in chloroform, less soluble in alcohol.

V. H. V.

Substituted Anthracene-γ-carboxylic Acids; Behaviour of Carbon Oxychloride towards Anthracene Dihydride. By G. Behla (*Ber.*, **20**, 701—708; compare Abstr., 1886, 248).—*γ-Chloranthracene-γ-carboxylic acid*, $C_{14}H_8Cl{\cdot}COOH$, is obtained by heating 3 grams of anthracene with 5—6 grams of carbon oxychloride for 6—7 hours at 240—250°; the product is extracted with boiling sodium carbonate solution, precipitated with hydrochloric acid, dried, and recrystallised from benzene, from which it separates in long, greenish-yellow, lustrous needles. It sublimes at 155°, and melts at 258—259°, with evolution of carbonic anhydride. It dissolves in alcohol, ether,

acetone, &c., sparingly in benzene and chloroform. The solutions have a blue fluorescence. Potassium permanganate and dilute nitric acid oxidise it to anthraquinone. Fuming sulphuric acid dissolves it with formation of a compound, crystallising in long, yellow needles, soluble in water; this is probably the disulphonic acid. *Potassium γ-chloranthracenecarboxylate*, $C_{14}H_8Cl{\cdot}COOK$, forms very slender, yellow needles; the *barium salt* crystallises in lustrous, yellow prisms. The *methyl salt* crystallises in tufts of slender, yellow needles, which melt at 123°; it is insoluble in water, soluble in alcohol, ether, and chloroform.

Methyl anthracene-γ-carboxylate, $C_{14}H_9{\cdot}COOMe$, forms yellow prisms, melting at 111°; it resembles the chlorinated derivative in its solubility.

γ-Chloranthracene-γ-carboxylic acid can be obtained by passing dry chlorine through a solution of anthracene-γ-carboxylic acid in chloroform; by the action of a second molecule of chlorine in the product, dichloranthracene, melting at 209°, is obtained.

γ-Bromanthracene-γ-carboxylic acid is prepared by adding the calculated amount of bromine to a solution of anthracene-γ-carboxylic acid in glacial acetic acid; the product is treated with water, filtered, and the precipitate warmed with sodium carbonate solution; it is again filtered, precipitated with hydrochloric acid, dried, and crystallised successively from benzene and alcohol. It forms greenish-yellow, lustrous needles, which sublime at 160°, and melt at 266°, with evolution of gas. It is almost insoluble in water, soluble in ether, alcohol, and glacial acetic acid. The solutions show a blue fluorescence. It dissolves in fuming sulphuric acid, forming a reddish-yellow solution with green fluorescence; a yellow crystalline substance is formed, probably a disulphonic acid. *Potassium-γ-bromanthracene-γ-carboxylate* forms very slender, long, yellow needles; the *barium* and *silver salts* crystallise respectively in lustrous needles and microscopic prisms; both are yellow.

Anthracene-γ-carboxylic acid monosulphonic acid, $COOH{\cdot}C_{14}H_8{\cdot}SO_3H$, is obtained by keeping a solution of the carboxylic acid in concentrated sulphuric acid surrounded by ice for 12 hours, and precipitating with water. It is purified by means of the barium salt. The free acid crystallises from alcohol in microscopic, slightly yellow prisms, which do not melt at 360°; it dissolves readily in water and alcohol, and is insoluble in ether and benzene. The aqueous solution shows a blue fluorescence. The *barium salt* is very readily soluble in water.

The *disulphonic acid*, $COOH{\cdot}C_{14}H_7(SO_3H)_2$, is prepared by dissolving the carboxylic acid in fuming sulphuric acid, and precipitating with water. It forms prisms, readily soluble in water and alcohol. The aqueous solution shows hardly any fluorescence; the solution in sulphuric acid has a yellowish-green fluorescence. The *barium salt* is very sparingly soluble.

When anthracene dihydride (Liebermann and Topf, this Journal, 1877, i, 86) is heated with carbon oxychloride at 200° for four hours, anthracene is regenerated; when the temperature is raised to 240°, and the heating continued for four hours, anthracenecarboxylic chloride and chloranthracenecarboxylic chloride are formed. N. H. M.

Nitrogen-derivatives of Terebenthene. By C. Tanret (*Compt. rend.*, **104**, 791—794).—The mother-liquor from terpin and the liquid hydrates formed from terebenthene by the action of nitric acid diluted with alcohol, were washed with water, neutralised, and distilled in a current of steam. The distillate consists of unaltered terebenthene, mixed with a continually increasing proportion of hydrate as the temperature rises. The nitrogen-derivatives are found in the last portions of the distillate. The liquid thus obtained is neutral to litmus, and colourless. With alcoholic potash, it yields potassium nitrite. A similar product is obtained by the action of nitric oxide on terpene hydrates, and hence it would seem that the compound is of the same nature as nitroethane, but less stable. When heated at 100°, it becomes acid, and decomposition increases as the temperature rises, and becomes rapid at 150°, nitrogen, nitric oxide, and water-vapour being given off.

The liquid product of the reaction is agitated with dilute soda, and the latter is treated with sulphuric acid and agitated with chloroform. When the chloroform is distilled, and the residue treated with boiling water to remove tarry matter, a crystalline substance is obtained, which is recrystallised from alcohol. Direct treatment of the washed and neutralised mother-liquor in the same way yields the same product.

The solid product is a mixture of two isomerides of the composition $C_{10}H_{17}NO_2$, which can be separated by means of ether. The α-compound is comparatively insoluble in ether, and requires 30 parts of this liquid for solution. It dissolves in 6 parts of alcohol of 90°, 20 parts of water at 100°, and 68 parts at 13°, and is very soluble in chloroform. It melts at 210°, boils at 283° with partial decomposition, and crystallises in long, brittle, opaque, flattened prisms with a rhomboidal base. The β-derivative crystallises in bulky, transparent, quadratic prisms, which begin to melt at 110°, are completely liquid at 114°, and boil at 274°. It appears to be a mixture of two isomerides. It dissolves in 7 parts of ether, 2·5 parts of alcohol, 7 parts of water at 100°, and 42 parts at 13°.

The rotary power of the α-compound is $[\alpha]_D = +69°$, of the β-compound $[\alpha]_D = +18·4°$. Both are neutral to litmus, but have a distinctly acid function. They are not affected by strong sulphuric acid, nor by a solution of potassium hydroxide, but when fused with caustic alkalis they yield an alkaline carbonate and cyanide. When heated with soda-lime, only 76 per cent. of the nitrogen is evolved as ammonia.

With ferric salts, they give a deep violet coloration, owing to the formation of a compound $(C_{20}H_{34}N_2O_4)_3(Fe_2O_3)_2$, which can be isolated. It dissolves in water, forming a reddish-brown solution which changes to red on addition of a trace of an organic acid.

If an excess of calcium saccharate is added to a solution of the α-compound, the salt $(C_{10}H_{16}NO_2Ca)_2 + 3H_2O$ is obtained in slender crystals, only very slightly soluble in water. C. H. B.

Terpenes and Ethereal Oils. By O. Wallach (*Annalen*, **238**, 78—89).—Schmidt (*Arch. Pharm.* [2], **141**, 1) and Oglialoro (this

Journal, 1876, ii, 642) have pointed out that oil of cubebs contains two sesquiterpenes, $C_{15}H_{24}$, one of which yields a crystalline hydrochloride, $C_{15}H_{24}2HCl$, melting at 117—118°. The author has succeeded in obtaining this hydrochloride from oil of cubebs, patchouli (b. p. 270—280°), oil of galbanum, *Oleum cadinum*, and *Oleum sabinæ*. It is best obtained by distilling *Oleum cadinum* in a current of steam, and treating the distillate with potash to remove phenols. The purified oil is distilled over potash, and the portion boiling between 260° and 280° is diluted with ether and saturated with hydrogen chloride. The hydrochloride can be recrystallised from ethyl acetate. It is deposited from ether in rhombic prisms, $a : b : c = 0{\cdot}61379 : 1 : 0{\cdot}41432$. The solution is lævogyrate. The terpene is easily obtained by heating the hydrochloride with anhydrous sodium acetate and acetic acid. The sesquiterpene boils at 274—275°. Its sp. gr. at 16° = 0·921. It has a great tendency to resinify. The hydrochloride, hydrobromide, and hydriodide are conveniently prepared by adding the corresponding acid to an acetic acid solution of the terpene. $C_{15}H_{24},2HBr$ melts at 124—125°. $C_{15}H_{24},2HI$ melts with decomposition at 105—106°. A solution of the terpene in a large excess of chloroform or acetic acid, gives on the addition of strong sulphuric acid first a green, and then a blue coloration. Attempts to prepare the sesquiterpene from isoprene were unsuccessful. W. C. W.

Ethereal Oils. By E. Weber (*Annalen*, **238**, 89—108).—Oil of rosemary not only contains camphor, borneol and a terpene, but also cyneol, $C_{10}H_{18}O$, which was discovered by Wallach and Brass in *Oleum cynæ* (Abstr., 1885, 171).

Oil of cardamoms begins to boil at 164°, and the temperature gradually rises to 220°. A small quantity of a crystalline compound, which melts at 60—61°, is left in the retort. The liquid distilling over below 170° consists of water, acetic and formic acids.

The oil contains *terpinene*, boiling at 179—182°, and another terpene, which boils at 180—183° (probably limonene or dipentene), and yields a hydrochloride which melts at 52°. The portion of the distillate coming over between 205° and 220° contains the compound $C_{10}H_{18}O$, which is probably identical with Wallach's *terpineol* (Abstr., 1886, 71). W. C. W.

Active Camphene and Ethyl-borneol. By G. Bouchardat and J. Lafont (*Compt. rend.*, **104**, 693—695).—The monohydrochloride, $C_{10}H_{17}Cl$, with a rotatory power $[\alpha]_D$ −28° 30′, obtained from French essence of terebenthene, was heated in sealed tubes at 150° with somewhat less than its own weight of fused potassium acetate dissolved in very strong alcohol. After 48 hours, the product was precipitated with water, fractionated in a vacuum, and the unaltered hydrochloride was again subjected to the same treatment, twice at 150°, and finally at 175°. The rotatory power of the camphene obtained at each operation was—

	$[\alpha]_D$.	
	155—158°	158—161°
First treatment	77° 30′	−80° 37′
Second treatment	−67 21	−69 8
Third „	−60 35	−59 40
Fourth „	−30 30	−34 30

At a high temperature the potassium acetate and acetic acid either render part of the camphene altogether inactive, or diminish the general activity of the whole. The effect of temperature is very marked; the reduction in rotatory power was only 9—10° in the first two operations at 150°, whilst it was 30° in the last operation at 175°.

In addition to the camphene, a certain quantity of some substance is formed which distils over with the hydrochloride. This is *ethylborneol*, $C_{10}H_{17}EtO$, isomeric with the compound obtained by Baubigny by the action of ethyl iodide and potassium hydroxide on borneol. It boils at 205—208° under ordinary pressure; sp. gr. at 0° = 0·9495; vapour-density, 5·8; rotatory power, $[\alpha]_D = +26° 3'$. It is not affected by potash, but if treated at 0° with a saturated solution of hydrochloric acid it forms a buttery mass, which when compressed yields a solid camphoraceous substance mixed with borneol and borneol hydrochloride. When heated at 100° with ten times its weight of saturated hydrochloric acid, ethylborneol is completely converted into ethyl chloride and inactive camphene hydrochloride. It is rapidly oxidised by ordinary nitric acid, with formation of camphor. C. H. B.

Determination of Position in the Pyrroline Series. By G. Ciamician and P. Silber (*Ber.*, **20**, 698—700); compare Abstr., 1886, 938).—When tribromacetylpyrroline, methyl tribromocarbopyrrolate, dibromacetylmethylpyrroline, and dibromodiacetylpyrroline are treated with nitric acid, dibromomaleïnimide is formed. In these compounds, the acetyl, methyl, or carboxyl must be attached to the carbon-atom next to nitrogen in the pyrroline-ring.

When brominated pyrrylene dimethyl diketone is heated with fuming nitric acid, dibromomaleïnimide is at once formed; if the reaction is allowed to take place at the ordinary temperature, *dibromomononitracetylpyrroline*, $NO_2{\cdot}C_4NHBr_2Ac$, is obtained. This crystallises in long needles melting at 206°. When dissolved in a mixture of sulphuric and fuming nitric acids at −18°, and precipitated with water, dibromodinitropyrroline, $C_4NHBr_2(NO_2)_2$ is formed, which changes at the ordinary temperature into dibromomaleïnimide. These reactions can only be explained by assuming that the acetyl-group is directly substituted by the nitro-group. N. H. M.

Tetraiodopyrroline. By G. Ciamician (*Gazzetta*, **16**, 543—548). —Tetraiodopyrroline, sold commercially under the name of "iodole," is readily obtained by the direct action of iodine on pyrroline; it forms yellow crystals, insoluble in water, sparingly soluble in alcohol. Its presence may be recognised by the action of concentrated sulphuric acid; this produces an intense green coloration, which after some

time turns to a dirty violet. Its alcoholic solution yields an intense red coloration with nitric acid. Its physiological and therapeutic actions resemble those of iodoform, over which it has the advantage of being odourless and less poisonous. It has been successfully applied in venereal, ulcerous, and suppurative lesions. V. H. V.

Reaction of Acetone with Pyrroline. By M. Dennstedt and J. Zimmermann (*Ber.*, **20**, 850—857).—When acetone and pyrroline are heated in presence of zinc chloride, *isopropylpyrroline*, $C_4\dot{N}H_4Pr^{\beta}$, is formed (compare Abstr., 1886, 1043) together with a subsidiary product. This compound, best purified by means of its potassium-derivative, is a colourless oil boiling at 173—175°, it has the odour of the substituted pyrrolines, and gives the pine-wood reaction. The isopropyl-group is attached to one of the carbon-atoms. Like ethyl pyrroline, it yields an *acetyl*-derivative, $C_4NH_3Pr^{\beta}Ac$, which crystallises in the monoclinic system; $a : b : c = 1{\cdot}7304 : 1 : 0{\cdot}5009$; it melts at 64°, and boils at 251°; its *silver*-derivative is a white crystalline mass. Isopropylacetylpyrroline, when heated with benzaldehyde, yields a *cinnamyl*-derivative, $C_4NH_3Pr^{\beta}{\cdot}CO{\cdot}CH:CHPh$, melting at 142—143°, and crystallising in the rhombic system; $a : b : c = 0{\cdot}7002 : 1 : 0{\cdot}3833$. Potassium isopropylpyrroline, when fused with potash, yields the corresponding salt of a carbopyrrolic acid, which melts with decomposition at 166°, and is readily soluble in water, alcohol, and ether; its *methyl* salt crystallises in silky, colourless needles, melting at 129°. Isopropylpyrroline resembles the 1 : 4 dimethylpyrroline as regards its reaction with hydrochloric acid, in which the salt of a new base is produced; attempts, however, to prepare the compound in a fit state for analysis were unsuccessful. V. H. V.

Synthesis of Pyridine Bases. By J. Plöchl (*Ber.*, **20**, 722—723).—Pyridines are formed by the action of aldehydes on concentrated solutions of ammonium chloride at a high temperature. Collidine was obtained from paraldehyde, and parvoline from propaldehyde. The reactions are analogous to those by means of which quinoline-derivatives are obtained from the hydrochlorides of primary amines and aldehydes, ketones, &c. N. H. M.

Cinchonic Acid. By W. Muthmann and J. U. Nef (*Ber.*, **20**, 636—638).—Inasmuch as the crystallographic measurements of the crystals of cinchonic acid obtained by the oxidation of α- and β-3′-phenolquinoline did not agree with Ditscheiner's data (*Annalen*, **173**, 84), the authors compared the specimens with cinchonic acid prepared by the oxidation of cinchonine and of monobromapocinchene, and found them to be identical. Cinchonic acid crystallises from hot concentrated solutions with 1 mol. H_2O, but when a dilute solution is allowed to evaporate spontaneously, crystals with 2 mols. of H_2O are obtained. The latter are triclinic; $a : b : c = 0{\cdot}74653 : 1 : 0{\cdot}81749$; $\alpha = 81° 37'$, $\beta = 120° 2'$, $\gamma = 86° 37'$. The following faces were observed: $\infty\bar{P}\infty$, $\infty\check{P}\infty$, 0P, $\infty P'$, $\check{P}'\infty$, the pinacoïds usually predominating. Ditscheiner's observations are therefore erroneous.

W. P. W.

Condensation Products of Acetone and Acetophenone with Aniline and Ammonia. By P. Riehm (*Annalen*, **238**, 1—29).—When acetone and aniline hydrochloride in the proportion of 2 mols. of the former to 1 mol. of the latter are heated at 180° in sealed tubes, marsh-gas is evolved, water is eliminated, and α-γ-dimethylquinoline and a tertiary base are produced. The dimethylquinoline has been previously described by the author (Abstr., 1885, 1246). The tertiary base, NPh : CMe_2, is a colourless liquid boiling between 227° and 229°. On exposure to air and light, it darkens in colour. Most of the salts of this base are very soluble in water and in alcohol.

A small quantity of a crystalline base which melts at 340°, and yields crystalline salts, is obtained by the action of acetophenone on aniline.

β-Collidine is formed together with marsh-gas and water, by the action of acetone on ammonium chloride in sealed tubes at 265°.

In the presence of zinc chloride, acetone acts on carbamide at 110—140°, yielding β-collidine and a base (probably $C_{16}H_{19}N$). The base forms colourless monoclinic needles. It melts at 119°, and boils about 320°. It is soluble in alcohol, ether, benzene, chloroform, and light petroleum. The salts of the base do not as a rule crystallise well. Their solutions are fluorescent.

Triphenylpyridine, $C_{23}H_{17}N$, is formed by the action of ammonia on acetophenone, in the presence of phosphoric anhydride. The base melts at 135°, and yields a crystalline platinochloride.

W. C. W.

4′-Phenylquinoline and the Derived Diquinolyls. By W. Koenigs and J. U. Nef (*Ber.*, **20**, 622—636).—When 4′-phenylquinoline (Abstr., 1886, 1045) is treated with nitric acid of sp. gr. 1·5, and the whole allowed to remain for 12 hours, the nitrates of three nitrophenylquinolines are obtained, termed α, β, and γ respectively; from these, after liberation of the bases, the α-derivative can be separated by fractional crystallisation from alcohol, in which it is the least soluble, and the separation of the β- from the γ-derivative can be effected by converting them into sulphates, and crystallising out the less soluble β-sulphate. The yield of the α-base is 50 to 60 per cent., that of the β-base 35 to 45 per cent., and that of the γ-base 5 per cent.

α-Nitro-4′-phenylquinoline, $C_9NH_6{\cdot}C_6H_4{\cdot}NO_2$, crystallises in snow-white flocks, melts at 187°, and is sparingly soluble in cold alcohol and ether. Its salts crystallise well, and are sparingly soluble in water. When reduced with stannous chloride and hydrochloric acid, it yields *α-amido-4′-phenylquinoline;* this crystallises in colourless glistening scales, melts at 150°, is volatile with decomposition, and dissolves readily in benzene, chloroform, and hot alcohol, but very sparingly in ether, the ethereal solution showing a violet-blue fluorescence. It forms two series of salts which are distinguished by their colour, the di-acid salts being colourless, whilst the monacid salts are intensely yellow, and have considerable tinctorial powers. *α-4′-Phenolquinoline*, $C_9NH_6{\cdot}C_6H_4{\cdot}OH$, is formed when the α-amido-derivative is diazotised. It crystallises in flat needles or prisms,

melts at 243°, is volatile without decomposition, and dissolves readily in alcohol and chloroform, very sparingly in benzene, and is almost insoluble in ether. The *potassium* and *sodium* salts are precipitated by a slight excess of alkali in colourless, glistening prisms, and give yellow solutions with water. Oxidation with chromic acid converts it into cinchonic acid. When fused with potassium hydroxide, α-4′-phenolquinoline yields a compound, probably a phenoloxyquinoline, which melts above 317°, shows no basic properties, and is sparingly soluble in all solvents.

β-Nitro-4′-phenylquinoline crystallises in colourless, hard needles, melts at 117—118°, and is readily soluble in alcohol, very sparingly soluble in ether. *β-Amido-4′-phenylquinoline* crystallises in pale-yellow, four-sided prisms, melts at 198°, volatilises without decomposition and is soluble in chloroform, sparingly soluble in alcohol and benzene, and almost insoluble in ether, the ethereal solution showing a characteristic bluish-violet fluorescence. The monacid salts are intensely yellow, and have considerable tinctorial powers, whilst the di-acid salts are colourless. *β-4′-Phenolquinoline*, obtained by diazotising the β-amido-derivative, is granular, melts at 235°, volatilises without decomposition, and is sparingly soluble in alcohol, chloroform, and ethyl acetate, almost insoluble in ether. Aqueous potash and soda do not precipitate the corresponding salts. Oxidation with chromic acid converts β-4′-phenolquinoline into cinchonic acid. When fused with potassium hydroxide, *β-4′-phenoloxyquinoline*, $C_9NH_6O\cdot C_6H_4\cdot OH$, is obtained; this crystallises in pale-yellow needles, melts at 305°, sublimes unchanged, is readily soluble in alcohol and acetic acid, sparingly soluble in ethyl acetate, and is destitute of basic properties.

γ-Nitro-4′-phenylquinoline forms tabular crystals, melts at 135°, and is readily soluble in alcohol, sparingly soluble in ether. Its salts are readily soluble in water. The *amido*-derivative melts at 115°, and the corresponding *hydroxy*-derivative melts at 205°.

α-4′-Diquinolyl is prepared from α-amido-4′-phenylquinoline by Skraup's reaction. It crystallises in pale-yellow forms, melts at 122°, volatilises without decomposition, and is readily soluble in alcohol, soluble in chloroform, benzene, and ethyl acetate, very sparingly soluble in ether. Its salts are mostly readily soluble in water; the *platinochloride*, $C_{18}H_{12}N_2,H_2PtCl_6$, forms granular crystals, and is insoluble in water.

β-Diquinolyl is obtained by Skraup's reaction from β-amido-4′-phenylquinoline. It forms colourless, tabular crystals, melts at 116—117°, volatilises without decomposition, and is readily soluble in alcohol, soluble in chloroform, benzene, and ethyl acetate, very sparingly soluble in ether. Its salts are mostly readily soluble in water; the *platinochloride*, $C_{18}H_{12}N_2,H_2PtCl_6$, crystallises in yellow needles, and is insoluble in water. The mode of formation of these diquinolyls shows that each must have one of the four possible formulæ 4′ : 1, 2, 3, or 4.

The marked similarity in the properties of apocinchene (Abstr., 1882, 224) and the 4′-phenolquinolines renders it probable that the former is also a 4′-phenolquinoline, and the conjecture is further

strengthened by the fact that oxyapocinchene, obtained by fusing apocinchene with sodium hydroxide (*Ber.*, **18**, 2385), and the 4′-phenoloxyquinolines show similar properties. W. P. W.

Ortho- and Meta-quinolinesulphonic Acids. By O. Fischer (*Ber.*, **20**, 731).—Referring to La Coste and Valeur's paper (this vol., p. 379) the author points out that he and Bedall did not state that the solubility of ortho- and meta-quinolinesulphonic acids was identical, but merely that the difference was not sufficient to enable them to be thoroughly separated by simple crystallisation. He also states that as the meta-acid has recently been found to yield a quinolinecarboxylic acid with the carboxylic-group in the ana-position, it should now be called anaquinolinesulphonic acid. L. T. T.

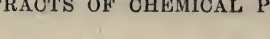
Synthetical Experiments by means of Ethyl Acetoacetate. By L. Knorr (*Annalen*, **238**, 137—219).—Many of the compounds obtained by the action of ethyl acetoacetate and its derivatives on the primary aromatic hydrazines have already been described by the author as *quinizines* (Abstr., 1884, 302, 1153, 1377, 1380, and 1381). The author now regards these substances as *pyrazolones*. Phenylmethylpyrazolone has the constitution $PhN<\begin{matrix}CO\cdot CH_2\\N:CMe\end{matrix}>$.

The *hydrochloride*, $C_{10}H_{10}N_2O,HCl + H_2O$, melts at 96°, and the *platinochloride*, $(C_{10}H_{10}N_2O)_2,H_2PtCl_6 + 4H_2O$, crystallises in prisms melting at 110°. The addition of silver nitrate to an aqueous solution of phenylmethylpyrazolone precipitates a crystalline double salt of the composition $C_{10}H_9AgN_2O + C_{10}H_{10}N_2O$.

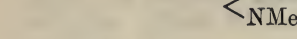
By the action of methyl iodide on the sodium salt of phenylmethylpyrazolone two atoms of hydrogen may be successively displaced by methyl, but *antipyrine* is formed when methyl iodide acts on a solution of phenylmethylpyrazolone in methyl alcohol at 100°. The constitution of antipyrine is $CO<\begin{matrix}CH=CMe\\NPh\cdot NMe\end{matrix}>$.

Phenyldimethylpyrazolone does not yield a nitro- or a nitroso-derivative. Nitrous acid oxidises this substance and converts it into *dis-phenyldimethylpyrazolone*, $C_{22}H_{22}N_2O$. Phenylmethylethylpyrazolone and its derivatives have been previously described (*loc. cit.*, p. 1380). *Phenyltrimethylpyrazolone*, $Ph:Me:Me_2 = 1:3:4$, formed by the action of phenylhydrazine on ethylic dimethylacetoacetate, melts at 55—56° and boils at 300—303°. It is soluble in alcohol, ether, benzene, and chloroform and in strong acids. From the acid solutions, it is precipitated on dilution with water. It is distinguished from its isomeride methylantipyrine by its volatility in a current of steam. Phenyltrimethylpyrazolone is converted into a base (probably phenyltrimethylpyrazoline) by treatment with sodium and alcohol. The dilute acid solution of the product yields an intense carmine coloration with a drop of ferric chloride.

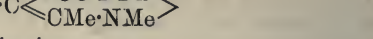
The preparation of dis-phenylmethylpyrazolone and its conversion into *di-antipyrine* and *pyrazol-blue* has already been described (*loc. cit.*, 1379).



Di-antipyrine.



Dis-phenylmethylpyrazolone [1 : 3 : 5].



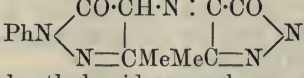
Pyrazol-blue.

Dis-phenyldimethylpyrazolone, $C_{22}H_{22}N_4O_2$ [1 : 3 : 4 : 5], is prepared by adding a solution of a nitrite to phenyldimethylpyrazolone dissolved in sulphuric acid. It crystallises in prisms and melts at 164°. It is soluble in alcohol and acetic acid. *Dis-phenylmethylethylpyrazolone*, [1 : 3 : 4 : 5] $C_{24}H_{26}N_4O_2$, melts at 160°.

On the addition of bromine to an acetic acid solution of phenylmethylpyrazolone [1 : 3 : 5], a monobromo-derivative is obtained. It melts at 128—130° and dissolves freely in chloroform and acetic acid. The alcoholic solution soon deposits pyrazol-blue, even at the ordinary temperature. The dibromo-derivative $C_{10}H_8N_2OBr_2$ melts at 80°; it is soluble in alcohol, ether, chloroform, and acetic acid. It is not attacked by oxidising agents, but is reduced by hydriodic acid or by tin and hydrochloric acid, yielding phenylmethylpyrazolone.

The dichloro-derivative $C_{10}H_8N_2OCl_2$ is best prepared by the action of phosphorus pentachloride on phenylmethylpyrazolone. It melts at 61°, and decomposes on boiling.

Benzaldehyde acts on phenylmethylpyrazolone, forming *phenylmethylbenzylidenepyrazolone*, $C_3N_2MePhO : CHPh$. This substance crystallises in orange-coloured prisms; it melts at 106—107°. *Phenylmethylcinnimenepyrazolone*, $C_3N_2MePhO : C_3H_3Ph$, melts at 139°. *Phenylmethylisopropylenepyrazolone*, $C_3N_2MePhO : CMe_2$, forms yellow needles which melt at 117°. It is soluble in ether, benzene, chloroform, alcohol, and strong acetic acid. *Phenylmethylpyrazoloneazobenzene* is obtained in orange-coloured needles when diazobenzene chloride is added to a cold solution of phenylmethylpyrazolone in acetic acid. The compound melts at 155°. The preparation of *phenylmethylisonitrosopyrazolone*, $C_3N_2MePhO : NOH$, has been previously described (*loc. cit.*, p. 1378). It melts at 157°. On careful oxidation with nitric acid, it is converted into *phenylmethylnitropyrazolone* (m. p. 127—130°). On reduction with zinc and acetic acid, both these compounds yield phenylmethylamidopyrazolone, $C_3N_2HPhMeO{\cdot}NH_2$ [1 : 3 : 4]. The *hydrochloride*, $C_{10}H_{12}N_3O,HCl$, forms colourless crystals. In solution, this salt rapidly oxidises to rubazonic acid. The *benzylidene*-derivative, $C_{17}H_{15}N_3O$, melts at 186° and dissolves in alcohol and chloroform with an intense yellow coloration.

Rubazonic acid,  , is formed by the oxidation of phenylmethylamidopyrazolone and also by boiling pyrazol-blue with dilute ammonia. It is insoluble in water and dilute acids, but dissolves freely in benzene, ether, and chloroform. It dissolves in alkalis with a deep-violet coloration. The alkali salts are

soluble in water but insoluble in solutions of caustic alkalis. The violet-colour changes to yellow when the alkaline solutions are boiled, and phenylmethylketopyrazolone and diphenylhydrazineacetylglyoxylic acid are probably formed. The latter compound melts at 212°, dissolves in alkalis, and dyes silk yellow. Phenylhydrazinephenylmethylketopyrazolone is formed when equivalent quantities of rubazonic acid and phenylhydrazine are boiled together in acetic acid. The compound crystallises in golden needles and melts at 155°.

On distillation with zinc-dust, phenylmethylpyrazolone yields aniline, benzene, ammonia, methyl cyanide, and phenylmethylpyrazine, C_3N_2HPhMe [1 : 3]. *Antipyrine*, $C_3N_2HPhMe_2O$ [Ph : Me_2 = 1 : 2 : 3], has been already described (Abstr., 1884, 1153, 1378). The *picrate* melts at 188°. The *ferrocyanide* and the *platinochloride*, $(C_{11}H_{12}N_2O)_2,H_2PtCl_6 + 2H_2O$, crystallise in prisms. Ferric chloride gives a deep brownish-red coloration with a neutral solution, and sodium nitrite gives an intense emerald coloration with a slightly acid solution of antipyrine. The formation of *methylantipyrine*, $C_3N_2PhMe_3O$ [1 : 2 : 3 : 4], has already been mentioned. This substance melts at 82—83°, and boils at 286° under 153 mm. pressure. The base is freely soluble in water, alcohol, and chloroform. The aqueous solution gives a violet-red coloration with ferric chloride and a white precipitate with potassium ferrocyanide. The picrate melts at 94°. *Di-antipyrine*, $C_3N_2PhMe_2O - C_3N_2PhMe_2O$, prepared by the action of methyl iodide and methyl alcohol on *dis-phenylmethylpyrazolone*, melts at 245° and dissolves freely in chloroform. The *picrate* is deposited from alcohol in needles and melts at 161°; the *hydrochloride*, $C_{22}H_{22}N_4O_2,2HCl + 2H_2O$, forms monoclinic crystals. The *platinochloride* crystallises in prisms and melts about 232—236° with decomposition.

The nitroso-, nitro-, and benzylidene-compounds have been previously described (*loc. cit.*). *Antipyrine dibromide*, $C_{11}H_{12}N_2OBr_2$, is formed when bromine is added to a solution of antipyrine in chloroform. It is unstable and easily loses hydrobromic acid, forming bromantipyrine. It is soluble in alcohol and chloroform and melts about 150°. *Bromantipyrine*, $C_3N_2PhMe_2OBr$, is deposited from hot water in needles, and is soluble in alcohol, chloroform, and hot toluene. The compound melts at 117°. W. C. W.

Alkaloïds. By O. de Coninck (*Compt. rend.*, **104**, 513—515).—Equal volumes of sparteïne, alcohol, and ethyl iodide heated together in sealed tubes at 100° for several hours yield needles of the ethylspartylammonium iodide, $C_{15}H_{27}EtN_2I_2$, described by Mills. The corresponding methyl-derivative forms white crystals. If either of these compounds is dissolved in a slight excess of warm alcohol, the solution rapidly becomes rose-coloured, but if some drops of potassium hydroxide solution of 45° are now added, no deep coloration is produced. It follows that sparteïne differs from the pyridines and dipyridines.

Nicotine reacts readily with ethyl iodide and yields a yellow, translucent solid which dissolves in warm, absolute alcohol, forming a deep-brown solution. If this is mixed with potash of 45°, and heated on a water-bath for 10 hours, a garnet-red coloration is produced which

afterwards changes to carmine. When the solution is mixed with an excess of hydrochloric acid and is poured into acidified water, there is no change of colour and no fluorescence, but after 24 hours the liquid becomes yellow.

It is evident from this behaviour that nicotine is related to the pyridic and dipyridic alkaloïds. C. H. B.

Strychnine. By C. Stoehr (*Ber.*, **20**, 810—814).—In order to obtain evidence on the view of Hanssen that strychnine contains a phenylpyridine-group as well as a quinoline-group (this vol., p. 505), the author has distilled strychnine with alkali and obtained, in addition to a hydride of pyridine, not fully examined, γ-picoline, identified by analyses of its auro- and mercuro-chlorides, and crystalline form, as also by the melting point of the latter. Experiments to obtain methyl chloride as a product of the decomposition of strychnine were unsuccessful. It is shown that strychnine does not contain a hydroxyl-group, in that by treatment with phosphorus pentachloride the atoms of oxygen remain intact, whilst three hydrogen-atoms are displaced by chlorine to form a *trichloro*-derivative, $C_{21}H_{19}Cl_3N_2O_2$, the hydrochloride and sulphate of which crystallise in leaflets. V. H. V.

Phenylpiperidine. By E. Lellmann (*Ber.*, **20**, 680—681).—*Phenylpiperidine*, $C_5NH_{10}Ph$, is obtained by heating bromo- or iodobenzene with piperidine (3 mols.) at 250—270° for several hours. Piperidine hydrobromide (or hydriodide) is formed at the same time. Phenylpiperidine is slightly heavier than water and reacts strongly alkaline.

Dinitrophenylpiperidine is readily prepared by the action of orthoparadinitrochlorobenzene on piperidine. It crystallises from alcohol in orange-coloured needles melting at 92°. From nitroparadichlorobenzene a compound, probably chloronitrophenylpiperidine, is obtained; it forms small red plates which melt at 51°.

Paranitrophenylpiperidine, $C_5NH_{10}{\cdot}C_6H_4{\cdot}NO_2$, is prepared by heating parachloronitrobenzene (1 mol.) with piperidine (2 mols.) at 120° in a reflux apparatus. The product is treated with moderately strong hydrochloric acid, filtered, and precipitated with ammonia. It crystallises from hot alcohol in very large, yellow plates melting at 105°. The *platinochloride* was prepared. *Amidophenylpiperidine*, $C_5NH_{10}{\cdot}C_6H_4{\cdot}NH_2$, is obtained by reducing the nitro-compound with tin and hydrochloric acid. It is obtained from its ethereal solution as a crystalline mass melting at 40°. N. H. M.

Berberine Salts. By C. Schilbach (*Arch. Pharm.* [3], **25**, 155—164).—The results obtained by the analysis of various berberine salts confirm the observations of previous investigators as to the composition of the alkaloïd and its salts, except in the case of the hydrochloride, which is shown to have the composition indicated by the formula $C_{20}H_{17}NO_4,HCl + 4H_2O$. J. T.

Action of Potassium Permanganate on Berberine. By E. Schmidt and C. Schilbach (*Arch. Pharm.* [3], **25**, 164—170).—Berberine, under the action of concentrated nitric acid, yields a tribasic

nitrogenous acid, berberonic acid, $C_5H_2N(CO\cdot OH)_3$, as has been shown by Weidel, and again by Fürth. It is remarkable that the principal effect of the action of potassium permanganate on berberine should be the production of a non-nitrogenous acid analogous to hemipinic acid, as J. Court has shown in an investigation instigated by one of the authors. The authors in supplementing this investigation, conducted the oxidation in an alkaline solution, and in general followed the course taken by Court. A hot dilute solution of berberine was treated with aqueous potash and then with hot potassium permanganate solution. The slight excess of permanganate was decomposed by a few drops of alcohol. Preliminary tests indicated the formation of only very minute quantities of oxalic acid. On the contrary, carbonic anhydride was freely evolved on adding excess of sulphuric acid, and a strong odour of nitric acid was perceptible. The filtrate from the manganese oxide was neutralised with sulphuric acid, evaporated to dryness, powdered, well shaken with ether, and treated with excess of moderately dilute sulphuric acid. On distilling off the ether, a brown liquid remained which deposited a considerable quantity of crystals when placed over sulphuric acid. To avoid loss, the brown liquid was dissolved in water and the contained acids were precipitated by means of a slight excess of lead acetate. The well-washed precipitate was treated with hydrogen sulphide, the lead sulphide and excess of hydrogen sulphide removed, and the liquid evaporated and set to crystallise over sulphuric acid. The filtrate from the lead precipitate was freed from acetic acid by repeated evaporation and again treated with lead acetate, when a further crop of crystals was obtained. The lead acetate treatment gave crystals much purer than those obtained by direct crystallisation of the ether extract. These crystals, dried at 100°, have a constant melting point of 160—162°, and amount to about 30 per cent. of the original berberine. A small quantity of nitrogenous, nodular crystals was obtained by treating the mother-liquor of the ether extract with water, dissolving the precipitate obtained in hot water, and purifying with the aid of lead acetate. No other well characterised compounds were isolated. A considerable portion of the nitrogen of berberine was evidently converted into nitric acid during the oxidation. Another portion appeared in the form mentioned above. A further portion was converted into ammonia, or at least into compounds which gave ammonia on distillation with potash. The copious oxidation product melting at 160—162°, obtained as above, was compared with hemipinic acid, specially prepared by Schilbach from narcotine, and the two compounds were shown to be identical. J. T.

Lactucerin. By G. Kassner (*Annalen*, **238**, 220—228).—Lactucerin can be obtained in a pure state by treating the ethereal solution with an aqueous solution of potassium hydroxide. Alcohol is then added to the ethereal extract, until a small precipitate forms. On the addition of water to the filtrate, lactucerin is deposited in white, microscopic, needle-shaped crystals. Lactucerin purified in this manner melts at 200°, but after it is purified by sublimation in an atmosphere of carbonic anhydride it melts at 210°. The results of

analyses agree with the formula $C_{28}H_{44}O_2$ more closely than they do with Hesse's formula $C_{20}H_{32}O_2$ (Abstr., 1886, 1020). On fusion with potash, hydrogen is evolved and *lactucol*, $C_{13}H_{20}O$, is formed according to the equation $C_{28}H_{44}O_2 + 2H_2O = C_2H_4O_2 + 2C_{13}H_{19}\cdot OH + 2H_2$. Lactucol melts at 160—162°, and crystallises in needles. The acetate melts at 198—200°. Solutions of the alcohol and of the acetate in ether, chloroform, and carbon bisulphide are dextrogyrate. These results differ in some important respects from those of Hesse (*loc. cit.*). W. C. W.

Cholic Acid. By F. Mylius (*Ber.*, **20**, 683—688; comp. Abstr., 1886, 480, 952).—*Iodocholic acid*, $(C_{20}H_{40}O_5I)_4,KI + xH_2O$, is obtained by adding a concentrated aqueous solution of 1 gram of potassium iodide to a solution of 2 grams of cholic acid and 0·8 gram of iodine in 40 c.c. of alcohol. The mixture is gradually diluted with water until the blue substance separates. This is then collected and washed with water. It forms a matted mass of a bronze-like lustre. When suspended in water (500 c.c.), an indigo-blue liquid is produced. When the latter is heated, it becomes yellow and cholic acid separates; when a few drops of the blue liquid are poured into water, the blue colour disappears in a few moments, and the solution is found to contain free iodine. The substance is therefore decomposed by excessive dilution. Sulphurous acid decolorises the liquid with separation of cholic acid. The solution is also decolorised by adding a few drops of soda solution, with formation of sodium cholate, iodide, and iodate; on adding hydrochloric acid, the blue compound is re-formed. When iodocholic acid is dried in a vacuum, a dark, lustrous, crystalline powder is obtained which dissolves in ether containing alcohol, yielding a yellow solution; this, when evaporated, leaves a yellow, amorphous substance which is anhydrous iodocholic acid. The latter becomes blue in presence of water.

The *compound* $(C_{24}H_{40}O_5I)_4,HI$ is prepared by adding a small quantity of hydriodic acid to the brown solution of cholic acid and iodine. The liquid at once becomes blue. The compound is isolated in a manner similar to the potassium compound which it completely resembles. The *barium compound*, $(C_{24}H_{40}O_5I)_8BaI_2$, and the zinc, cadmium, and ammonium compounds are obtained by using corresponding iodides in the place of potassium or hydrogen iodides.

N. H. M.

Bile Acids. By C. Schotten (*Zeit. physiol. Chem.*, **11**, 268—276).—The author has previously suggested (Abstr., 1886, 565) that the smaller solubility of the salts of cholic acid obtained from human bile as compared with those from the ox, was due to an admixture of choleates. Further researches have led to the conclusion that the second acid in human bile is neither choleïc acid, $(C_{25}H_{42}O_4)$, nor the desoxycholic acid $(C_{24}H_{40}O_4)$ of Mylius (Abstr., 1886, 480), although both of these resemble the second acid of human bile in the insolubility of their barium salts, but a previously undescribed acid of the formula $C_{23}H_{40}O_4$, and to which the name *fellic acid* is given. The insoluble barium precipitate was decomposed by boiling with sodium carbonate, the filtered solution shaken with ether, and then the free

acid obtained by means of hydrochloric acid. The barium salt, $(C_{23}H_{39}O_4)_2Ba$, contains 4 mols. H_2O, and is soluble in about 700 or 800 times its weight of water; the magnesium salt, $(C_{23}H_{39}O_4)Mg + 2\frac{1}{2}H_2O$, was also prepared; from both of these salts, the free acid was obtained. Fellic acid is not homologous with cholic or choleic acid, the nature of its relations to lithofellic, hyocholic, and chenocholic acids, requires further investigation. In the dry condition, it is strongly electrical, as shown by rubbing it with a pestle. With Pettenkofer's reaction, it gives a red but not a violet colour. It melts at 120°. By heating strongly, it yields a turpentine-like residue. Its taste is bitter.

In opposition to Mylius (Abstr., 1866, 952), the author adheres to the statement he previously made that cholic acid does not give an acetyl compound. W. D. H.

The Behaviour of Hydrogen Peroxide to Albumin. By C. Wurster (*Ber.*, **20**, 263—267).—Egg albumin is not affected by hydrogen peroxide when in an alkaline or neutral solution, but in an acid solution in the presence of sodium chloride, hydrogen peroxide causes the albumin in a few minutes or hours to be changed into a proteïd, insoluble in water. The rate at which this coagulation occurs varies directly with the fresh condition of the albumin, the concentration of the liquid, and especially the temperature, the most favourable temperature being from 37° to 40°, the mixture being kept in an incubator. For the precipitation, an equal volume of hydrogen peroxide is well shaken with the white of egg, and 1 to 2 c.c. of commercial lactic acid, and 1 to 2 grams of sodium chloride, or 20 c.c. of a 5 per cent. solution added for every 100 c.c. of albumin. The cold mixture remains clear, becomes cloudy when held in the hand, and after 12 hours in the incubator has set into a firm cheesy mass. It is not necessary to use so large an excess of hydrogen peroxide; 3 to 5 c.c. will often suffice, but 1 c.c. to the 100 of albumin does not cause complete coagulation. The mother-liquor has a greenish-yellow colour like whey; on evaporating it an acid syrup is obtained, which after repeated drying and heating is found to contain hydrogen peroxide. Alcohol precipitates a peptone-like substance from this syrup. The precipitate caused by the peroxide reminds one more of acid albumin than caseïn. On digestion with artificial gastric juice, it is rapidly and very completely peptonised. It is soluble in solutions of sodium carbonate; on neutralising this solution with acetic acid, a proteïd is precipitated, which blackens an alkaline lead solution, and is insoluble in sodium acetate or tartrate, and is, therefore, not the oxyproteo-sulphonic acid of Brücke and Maly. It is insoluble in salt solutions and in water, soluble in hot alcohol, for the greater part soluble in sodium carbonate solution and in concentrated acids in the cold, wholly soluble in sodium carbonate solution and dilute acids at a temperature of 70—80°. It is soluble with ease in caustic alkalis, especially in ammonia.

The precipitate caused by hydrogen peroxide is stated to be a mixture of gelatinous acid albumin with a large quantity of a proteïd very similar to caseïn.

In order to obtain the precipitate, acid, sodium chloride, and hydrogen peroxide must all be present, but acetic, phosphoric, or sulphuric acids may be substituted for lactic acid.

Lactic acid and sodium chloride are both present in sweat, and hydrogen peroxide can also be shown to be present by the tetramethylparaphenylenediamine paper test; as it is also in certain tissues; the question arises whether the deep cutaneous tissues are able by this means to cause coagulation of proteïds circulating in the lymph; this and the questions whether the coagulation of blood and of muscle plasma and the formation of caseïn in milk may be similarly explained, are not yet considered proven. W. D. H.

Deterioration of Diastase by the Action of Heat. By E. Bourquelot (*Compt. rend.*, **104**, 576—579).—A solution of diastase is heated at 68° for several hours, and is then allowed to act on potato starch. The enfeebled diastase, even when employed in large excess, has lost the power of carrying the hydration of the starch to its utmost limit, but accomplishes the first stages of the alteration with practically the same rapidity as natural diastase. It would seem that it is not the quantity of the ferment which is diminished, but its quality which is altered. It may, however, be supposed that natural diastase is a mixture of two or more soluble ferments, which are successively destroyed by the action of heat. C. H. B.

Physiological Chemistry.

Specific Gravity of Human Blood. By E. L. Jones (*J. Physiol.*, **7**, 1—14).—The observations were made by Roy's method (*Proc. Physiol. Soc.*, 1884). A drop of blood is introduced into a mixture of glycerol and water of known specific gravity; if the drop tends to rise or sink it is assumed that it is of lower or higher specific gravity respectively than the liquid in which it is placed. By having ready to hand a number of solutions of glycerol and water of different specific gravities, it was not difficult to find one in which the drop of blood neither rose nor sank, and as its specific gravity was known, the specific gravity of the blood examined was thus found. Fermentation changes are prevented in the standard solutions by adding to them either thymol or mercuric chloride.

The principal results obtained were as follows:—

1. The specific gravity is highest at birth, at a minimum between the second week and the second year, and rises gradually to a point attained in the male between the ages of 35 and 45, in the female after the climacteric.

2. The specific gravity of the blood tends to be higher in the male than in the female; and in the latter pregnancy diminishes it to a slight extent.

3. The immediate effect of mixed food is to cause a fall in specific gravity; but if alcohol is taken this effect is not observed.

4. Exercise if gentle causes a fall; if violent leading to perspiration, it causes a rise in specific gravity.

5. The specific gravity of the blood in a passively congested part of the body is higher than elsewhere.

6. Diurnal variation. The specific gravity of the blood tends to fall during the day and to rise during the night. W. D. H.

Causes of the Alteration of Blood in Contact with Air, Oxygen, and Carbonic Anhydride. By A. Béchamp (*Compt. rend.*, **104**, 587—589).—Separate quantities of blood were treated with (1) a current of ordinary air, (2) a current of air washed with water, (3) a current of pure, washed oxygen, and (4) the air was expelled by means of carbonic anhydride, and the vessel closed.

In no case, even after a month, did the blood acquire a disagreeable odour, although, as in the first experiment, it contained a large number of bacteria. Between 20° and 25° the blood in contact with air remains red, and deposits no crystals; that in contact with oxygen at 24—26° deposits some crystals after the second day, and their number slowly increases. The blood in contact with carbonic anhydride deposits no crystals at 20—28°, and the blood becomes dark-red; at 33—40° crystals appear, and the blood becomes brown. Addition of one-fourth the volume of a 0·2 per cent. solution of phenol accelerates the formation of these crystals. The destruction of the corpuscles is evidently not due to the action of oxygen, since it takes place most readily in presence of carbonic anhydride. The formation of the crystals and destruction of the corpuscles in presence of carbonic anhydride is a function of the temperature, and this is probably true also in presence of air or oxygen.

Other experiments show that none of the substances separated from blood, such as hæmoglobin and albumin, alter under the conditions described, and the changes observed in blood by Pasteur and by the author can only be due to the activity and influence of the microzymes in the blood. C. H. B.

A First Product of Gastric Digestion. By K. Hasebroek (*Zeit. physiol. Chem.*, **11**, 348—360).—When fresh fibrin is employed in experiments on artificial gastric digestion, it is found that previous to the formation of parapeptone or syntonin, and propeptone and peptones, there is a substance present which is a globulin. It is soluble in weak saline solutions, precipitable on dilution with water, by saturation with sodium chloride or magnesium sulphate, and can be separated by fractional heat coagulation into two proteïds which coagulate respectively at the temperatures 55° and 72°. Supposing fibrin to be formed from fibrinogen and serum globulin (Schmidt), the conclusion is drawn that the first effect of gastric juice or fibrin is to separate it into two substances, one of which corresponds exactly with one of the components of fibrin (serum globulin), and the other only differs from the other component of fibrin (fibrinogen) in

having lost the power of coagulating under the influence of the fibrin ferment.

If boiled fibrin be employed, no such globulins are formed in gastric digestion.

One experiment only was made with fibrin that had been kept under alcohol; from it a small amount of globulins was obtained by the action of artificial gastric juice; as, however, the fibrin had only been under alcohol for two days, it is probable that some uncoagulated fibrin was still present. Experiments with egg albumin coagulated either by heat or by alcohol, showed that no globulin was yielded by gastric digestion. Lastly, it was found by using a pure solution of trypsin, or at least one which contained no globulins, and subjecting fibrin freed from adherent globulins by washing it with a solution of ammonium chloride, to its action in an alkaline medium, that the first effect of tryptic digestion was exactly the same as that of gastric digestion. W. D. H.

Intestinal Digestion in the Horse. By H. Goldschmidt (*Zeit. physiol. Chem.*, **11**, 286—305).—The reaction of the contents of the small intestine of the horse was usually as follows:—At the duodenal end the reaction was acid; then after the first 15 to 20 inches neutral or weakly alkaline; in the remainder of the small intestine it was alkaline, and towards the end of the ileum strongly alkaline. The consistency was slimy, especially in the duodenum, the sliminess seeming to depend on the presence of starch; the colour depends on the food, but the colour of the intestinal juice is dark yellow, becoming darker brown down the intestine. The contents give the reactions of proteïds, peptones, and sugar, especially the latter; the amount present being on the average 0·5 to 1·5 per cent.

The digestion in the small intestine is in the horse not so important as in the stomach. Whilst in the stomach about 55 per cent. of the albuminous and about 40 per cent. of the non-nitrogenous constituents are digested, about 20 and 25 per cent. respectively represent digestion in the small intestine. During inanition an extraordinarily large quantity of fluid (4 to 6 litres) is present in the small intestine. With regard to the movement of the food, it was found that the first portions reached the colon about 8 to 12 hours after it was eaten. Digestion in the large intestine of the horse is not described.

W. D. H.

Oxidation in the Animal Body. By C. Wurster (*Ber.*, **20**, 256—263).—Certain amines being well adapted to the study of oxidation processes, the following experiments were performed:—

Tetramethylparaphenylenediamine was injected subcutaneously and into the veins of certain warm-blooded animals (rabbits, guinea-pigs, and pigeons), and soon caused the death of the animal after violent convulsions. Post-mortem examination gave in most cases a negative result; the base could not be discovered in the skin or muscles, as it had been oxidised to form a colourless substance. The liver and bile contained traces. Freshly captured frogs also oxidise the base quickly if its hydrochloride is employed. By using the acetate or sulphate subcutaneously, the muscles under the skin are seen during life to be

blue-violet. This colour is formed more quickly in the presence of air. The skin also contains the pigment, but appears to oxidise the colouring matter more slowly. After frogs have been kept a long time without food, their tissues burn the tetramethylparaphenylenediamine with greater difficulty, but better if muscular movements are brought about, and if a weak solution of sugar be added to the hydrochloride of the base. After intravenous injection of such a mixture into a frog, the unchanged substance is found after death in the liver, blood, bile, certain muscles, and the central nervous system, and the free base can be obtained by treating with sodium hydroxide and subsequent shaking with ether; treatment of the tissues with a solution of copper sulphate or of iodine gives a blue-violet coloration.

The liver in the air became deep-blue violet; certain muscles, especially of the trunk, also became violet, and darkened on exposure in the air; the muscles of the lower extremity which continued to move longest were free from colour, which they had probably oxidised. In the alimentary canal, the mucous membrane was colourless, marking it off sharply from the muscular coat, which became violet in the air. These facts show that protoplasm, although itself reducing, can on access of air bring about powerful oxidation, and that even after the death of the animal, further oxidation processes will go on in the cells which still retain vital power. Moreover, the organs which during life form glycogen, namely, the liver and resting muscles, produce oxidation only to a certain extent, whilst the acting muscles, the glands of the alimentary tract, and the skin, cause still further oxidation, resulting in the formation of a colourless compound from the amine.

Dimethylparaphenylenediamine behaves similarly to the tetra-compound, but as its oxidation occurs more slowly, the effects on warm-blooded animals can be observed better. 20 to 40 c.c. of a $\frac{1}{2}$ to 3 per cent. solution of the hydrochloride causes in warm-blooded animals violent convulsions and death, the symptoms much resembling those described by Brieger as the result of poisoning by tetanine. Weaker solutions do not kill so quickly; the muscles in certain cases became violet during life; and in these the base is no longer present as such; but as a rule in the muscles in the neighbourhood of the injection, and in certain cases in the tears and peritoneal fluid the base could be detected after treatment with sodium hydroxide and ether, or by the red colour produced by chromic and glacial acetic acids. In the lung, the blue oxidation product caused mottling, and both this organ and the muscle darkened as in the case of the tetra-compound on exposure to air. The blood contains the unaltered amine. Experiments on frogs gave confirmatory results. Muscle which had undergone heat rigor no longer produced oxidation changes; this is analogous to fibrin, which, as Scherer (*Annalen*, **40**, 15) showed, does not decompose hydrogen peroxide after it had been boiled. The general conclusions drawn are: (1) That during life oxidation processes go on in the body, corresponding with the effect produced by ordinary oxidising agents on di- and tetra-methylparaphenylenediamine, which, causing them to take up 1 atom of oxygen, produces a blue-violet colour; or they may undergo still further oxidation, 6 atoms of oxygen being used to form carbonic anhydride from two methyl-groups, and

so convert the amine into a colourless derivative; (2) the oxidation of the amines occurs not in the blood, but in the tissues; (3) the secretions of the body are also strongly oxidising, in virtue of the hydrogen peroxide they contain; (4) the rapidity with which dimethylparaphenylenediamine is burnt in the tissues, as compared with what occurs in laboratory experiments or in the secretions, points to oxidation in the tissues as being brought about by atomic oxygen, which is probably produced, as Hoppe-Seyer suggests, by the action of nascent hydrogen (Abstr., 1886, 120).

Many of the foregoing experiments and conclusions run counter to those of Ehrlich (*Das Sauerstoffbedürfniss des Organismus*, Berlin, 1885). Ehrlich's methods are criticised by the author. W. D. H.

The Fate of certain Chlorine Compounds in the Organism. By A. Kast (*Zeit. physiol. Chem.*, **11**, 277—285).—Certain results of Mylius, showing the influence of the administration of chloroform on the amount of chlorine in the urine of the dog, which have not been hitherto published, are first given. The following example will illustrate the result arrived at:—

Day.	Amount of urine.	Specific gravity.	NaCl.
1	700 c.c.	1010	0·1
2	950 „	1009	0·13
3	1050 „	1011	1·48
4	570 „	1012	0·44
5	570 „	1012	0·25

On the second day, 10 grams of chloroform were given; the next day's urine shows a great increase of sodium chloride. Ether given in similar amount produced no such change.

This research was now pursued further; the effect of the inhalation of chloroform was first tried on a dog. The following table shows the results obtained:—

Day.	Quantity of urine.	Specific gravity.	NaCl.	Remarks.
1	170	1035	0·11	
2	290	1038	0·25	Chloroform narcosis for 4½ hours.
3	290	1039	0·89	
4	210	1033	0·24	
5	270	1036	0·26	
6	160	1037	0·18	Deep ether narcosis for 4½ hours.
7	240	1036	0·26	
8	260	1036	0·20	

The effect in the increase of chlorides is thus seen to be very marked after chloroform narcosis; whilst ether produces no effect.

During the progress of the experiment, the animal was kept on a

constant diet containing as few chlorides as possible. Following out a similar experiment on man, it was found that chloroform narcosis here also produced an increase in the urinary chlorides.

Chloral was next investigated, and it was found to have no such effect in producing an increase in the chlorides of the urine; Mering has previously shown that this substance leaves the body as urochloralic acid, and does not part with its chlorine. Similar investigations with carbon tetrachloride, methyl chloride, and ethyl dichloracetate also gave negative results, but ethyl trichloracetate, on the other hand, produced a very decided increase in the output of chlorides. W. D. H.

Formation of Xanthocreatinine in the Organism. By A. Monari (*Gazzetta*, **16**, 538—543).—In the course of investigations on the changes produced by fatigue in the chemical composition of muscle, it was observed that the quantity of creatinine was one-third to one-half greater than that of creatine, and that the compound of creatinine with zinc chloride was precipitated in pale-yellow, acicular crystals. In the course of working up an extract of flesh, a yellow flocculent mass was obtained soluble in water and alcohol, from which it may be recrystallised. This substance was shown by analysis and by its physical and physiological properties to be identical with the xanthocreatinine isolated by Gautier.

The same substance was also extracted, together with creatinine, from the urine of soldiers after a march of several hours. Considerable difficulty was experienced in the complete separation of the xanthocreatinine from creatine. V. H. V.

Invertebrate Chromatology. By C. A. MacMunn (*Proc. Physiol. Soc.*, 1887, 11—12).—Chlorophyll is present in nine specimens of sea-water sponge in addition to the fresh water sponge, the presence of chlorophyll in which was shown by Ray Lankester. A histohæmatin soluble in glycerol was found in seven species; in some reddish sponges this is replaced by tetronerythrin or allied pigments. In most sponges, various lipochromes are present.

Hæmatoporphyrin occurs in all parts of the body of the mollusc *Solecurtus strigillatus*, except where it is attached to the shell. It is curiously distributed in the epidermis, being laid down at the margins of the cells, which are serrated, and reminding one of pavement epithelium stained with silver nitrate.

In *Anthea cereus*, chlorophyll is present, but in this case is due to the presence of symbiotic algæ. In *Flustra foliacea*, chlorophyll is present in the "brown bodies," which Moseley says are due to the atrophy of the zooids. As these "brown bodies" contain diatoms, &c., eaten by the zooid, it is possible that chlorophyll may in this case be derived from food products. Its spectrum, however, resembles that of enterochlorophyll. W. D. H.

Analysis of Nitrogenous Metabolites in Fæces. By A. Stutzer (*Zeit. physiol. Chem.*, **11**, 361—364).—The author has previously described (Abstr., 1886, 377) a method of separating the nitrogenous

constituents of fæces due to metabolism from those which are not, by means of artificial gastric juice, or better still by the successive action of gastric and pancreatic ferments. Pfeiffer has stated that the fæces must be used in the fresh, not in a dried condition, as the process of drying converts some of the nitrogenous constituents of the fæces into such a condition as to be indigestible. The fæces used in Pfeiffer's work had, however, been under alcohol for two years, and therefore it was deemed advisable to repeat the experiment. The fæces of the cow and horse were used, and the result of nitrogen estimations confirms the accuracy of Peiffer's statement as is shown by the following numbers:—

	Nitrogen left after peptic digestion.	Nitrogen left after peptic and pancreatic digestion.
Cow's fæces (fresh).....	50 per cent.	45 per cent.
Ditto (dry).....	69 ,,	51 ,,
Horse's fæces (fresh).....	47 ,,	30 ,,
Ditto (dry).....	49 ,,	34 ,,

W. D. H.

Proteïds of Cerebrospinal Fluid. By W. D. Halliburton (*Proc. Physiol. Soc.*, 1887, 14).—A few specimens of fluids obtained from meningocœles and from cases of chronic hydrocephalus were examined. It was found that all the proteïds were precipitable by saturation with magnesium sulphate. Serum albumin was therefore absent. The precipitate was redissolved and found to consist of a small quantity of serum globulin, but the greater part consisted of proto-albumose. In one case, a variety of albumose was present, which was not precipitable by magnesium sulphate or sodium chloride (deutero-albumose). In cases of acute hydrocephalus, the total quantity of proteïds in the cerebrospinal fluid was greater than normal, and the fluid contained serum albumin as well as serum globulin and albumose. The question as to whether a proteolytic ferment exists in the fluid has not as yet been investigated. A number of specimens of hydrocele, pericardial, peritoneal and pleuritic fluids were also examined for albumoses, but with negative results. Several specimens of human blood, and the blood of other mammalian animals were also examined, but no albumose was found in any of them.

This peculiarity of the proteïds of cerebrospinal fluid, together with the previously known facts of the existence of a substance in it which reduces alkaline solutions of cupric hydrate, and of the excess of potassium over sodium salts in the fluid, shows that effusions into the cerebrospinal cavity differ considerably from the other so-called serous effusions. W. D. H.

Therapeutic Action of Colchicine. By A. Mairet and Combemale (*Compt. rend.*, **104**, 515—517).—Experiments on men, dogs, and cats show that colchicine acts either as a diuretic or a purgative

according to the dose administered, and acts by irritating the kidneys and digestive canal. The effects are the same whether the drug is administered hypodermically or by ingestion, but the action is more rapid in the former case, and the effects are produced by smaller doses. Man is three times more sensitive to its action than are cats and dogs. A dose of 2 to 3 mgrms. is sufficient to produce the diuretic, and 5 mgrms. to produce the purgative action. Colchicine increases the excretions and produces congestion at the articulations and in the bony cartilage. Its tendency to accumulate in the organism, and its great toxic power, make it essential to use the greatest care in administering it. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Changes Induced in Water by the Development of Bacteria. By T. Leone (*Gazzetta*, **16**, 505—511).—The author has already demonstrated that the number of micro-organisms, in a typically pure water, such as the Maugfall near Munich, although at first small, yet on standing gradually increase to a maximum, and afterwards rapidly decrease. The development of bacteria induces certain chemical changes in the water; thus the quantity of oxidisable organic matter gradually decreases, whilst the proportion of ammonia increases to a maximum, and then decreases owing to its oxidation into nitrites and nitrates; on this account, the time which elapses between the taking of a sample and its analysis is an important factor. The consequent changes are divisible roughly into two distinct periods: the first, in which the organic matter is decomposed with production of ammonia; and the second, in which this is subsequently oxidised. It is further shown, on the other hand, that certain micro-organisms seem to act as reducing agents, reconverting the nitrates into ammonia, and even the same organisms, according to the conditions, may have either an oxidising or a reducing function. In the first phase, when the nutritive matter is readily oxidisable and assimilated, the micro-organisms thrive at its expense, the process of nitrification being materially assisted by atmospheric oxygen; in the second phase, on the other hand, the necessary oxygen is derived from the nitrates; thus a change, seemingly of reduction, is induced. V. H. V.

Formation of Albumin in Plants. By A. Emmerling (*Landw. Versuchs-Stat.*, 1887, 1—180).—This long paper is a report of a series of experiments made by the author in order to determine the locality in which, and the mode by which, vegetable albumin is formed: they are a continuation of previous experiments of his own, and a kind of test of those made by Kellner, Schultze, Hornberger, and others, abstracts of whose researches will be found in this Journal, 1879, 819; 1880, 279, 493, 731; 1883, 491; 1885, 1087.

Observers have adopted two hypotheses to account for the phenomena of the production of amido-compounds in plants. One that they are formed synthetically in the plant from inorganic nitrogenous matter and organic substances brought into contact with it; the second, that they are formed from the decomposition of albumin already existing in the plant.

Growing plants are rich in amido-acids, the quantity diminishes as the plants grow older, and young cells cease to be produced, the amides being specially their nutriment. Schultze (Abstr., 1883, 493) thinks that there is a constant process of decomposition and reformation. Hornberger, in his studies on the growth of the maize plant (Abstr., 1883, 491), and on that of *Sinapis alba* (Abstr., 1885, 1087) has thrown very great light on the subject; he is of the opinion that amido-compounds are formed according to the first hypothesis, but does not indicate the locality of their production.

The results of the author's experiments are given in tables which cover 46 pages. The plants used were the common bean, and the estimations comprised—total dry substance, total nitrogen, nitrogenous combinations soluble in aqueous potash, nitrogen existing as legumin, albumin, ammonia, amido-acids, amides, carbamides, and nitrates respectively, sulphur as sulphuric acid, and in organic combination.

There is an intimate and striking connection between the development of the leaves and the fruit of plants; when the leaf is growing, the production of nutrient matter is very active, but it is consumed by the leaf itself. When it has ceased growing, the same active production continues, but it is for the benefit of the seed or fruit, which only develops when the leaf is fully formed; the author believes that the leaf is the principal centre of albumin formation from whence it is diffused throughout the plant, the roots and stems playing a subordinate part in the process. In all parts of the plant, amido-acids are found, and it would seem that there are several centres of production.

The formation of new cellular matter in the first case is at the cost of the nitrogen stored in the seeds, and as the plant grows the quantity contained in the stem and roots sensibly diminishes.

The results of researches hitherto made are not decisive, however, although the author believes that the weight of probability is in favour of the synthesis of amido-compounds from inorganic and organic nitrogenous matter; he considers the difficulties of the alternate hypothesis too great, as it requires a regressive metamorphosis in presence of a most active production of the very matter which is being decomposed. The question, however, must still be considered an open one, as in recent experiments of Borodin and Schultze they observed that on many occasions cut plants placed in water for some time produced considerable quantities of asparagine and other amido-compounds which arise from the decomposition of albumin. J. F.

American Barley. By C. Richardson (*Amer. Chem. J.*, **9**, 16—22). Märcker found that the finest grain contained not more than 8 per cent. of albuminoïds, and consisted of at least 80 per cent. mealy kernels. Of 12 typical specimens of the Canadian crop, none

were below 9 per cent. of albuminoïds, the average being 9·83, and only 6 contained 60 per cent. of kernels mealy or half mealy in structure. The average amount of albuminoïds in the barley of the United States, 11·50 per cent., is still higher. The average of 127 specimens from all parts of the world is given by Koenig as 11·14 per cent. Winter grown barley contains less albuminoïds than spring-grown, namely, 10·05 as against 11·42 per cent. H. B.

Destruction of the Nematoïds of Beetroot. By A. Girard (*Compt. rend.*, **104**, 585—587).—When the nematoïds have not been long established and the area infected is limited, carbon bisulphide is an efficacious remedy, but must be applied in considerable quantity. Very satisfactory results were obtained by injecting it into the soil at a depth of 0·25 metre in the proportion of 300 grams per metre. Potassium thiocarbonate is of very little value as a remedy.

C. H. B.

Direct Absorption of Free Nitrogen from the Atmosphere by Vegetable Soils which are Supporting Vegetation. By Berthelot (*Compt. rend.*, **104**, 625—630).—The experiments were made with soils in which *Amarantus pyramidalis* was being grown. The nitrogen in the soil and in the roots of the plants were estimated at the outset, and the nitrogen existing in the rain-water and the ammonia in the atmosphere during the course of the experiments were also determined. The nitrogen in the water which drained from the soil was estimated, and at the close of the experiments the nitrogen existing in the plants and in the soil was determined. In all cases there was a very decided gain of nitrogen, which could only have been derived from the gaseous nitrogen of the atmosphere.

The increase of nitrogen whilst the soil is supporting vegetation is less than in the case of the same soil on which nothing is being grown. The plants consume a considerable part of the nitrogen, and it would seem that the life of higher plants like that of higher animals causes an incessant loss of combined nitrogen. Further experiments are, however, required before this last conclusion can be regarded as placed beyond doubt. C. H. B.

Incompatibility of Nitrates and Superphosphates. By A. Andouard (*Compt. rend.*, **104**, 583—585).—Mixtures of nitrates with superphosphates very rapidly lose their nitric nitrogen in the form of nitrogen oxides, and therefore still more rapidly when exposed on the surface of the soil to direct solar radiation. At the same time, there is some loss of organic nitrogen, and if the manure also contains ammonium salts there is likewise a loss of ammoniacal nitrogen.

C. H. B.

Analytical Chemistry.

Behaviour of Alkaline Solutions of Phenolphthaleïn in the Presence of Alcohol. By H. N. Draper and C. Draper (*Chem. News*, **55**, 133—134; 143—144).—The authors have investigated the conditions influencing the decolorisation of slightly alkaline solutions of phenolphthaleïn by the addition of alcohol; it would appear that dissolved carbonic acid is in the main the cause of the phenomenon. D. A. L.

Apparatus for Estimating Hydrogen in the Presence of Methane. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **11**, 257—267).—This is a modification (figured) of Winkler's apparatus, in which (1) the mixture of gases is collected over mercury; (2) the portion of gas which has been freed from hydrogen by the action of palladium is transferred without loss to a eudiometer for further investigation. After this, the apparatus is ready for a fresh analysis. W. D. H.

New Method of Standardising Iodine Solutions and of Estimating Sulphurous Acid in the Presence of Thiosulphuric Acid. By W. Kalmann (*Ber.*, **20**, 568—570).—If sodium sulphite is employed instead of hydrogen sulphide in titrating iodine solutions (Abstr., 1886, 579), the objections to the method arising from the use of the gas and the deposition of finely divided sulphur are removed. The sodium sulphite must be free from sodium hydrogen sulphite and from sodium carbonate, and a solution containing 15 grams in the litre is a convenient strength to employ. This is added to the iodine solution until it is just decolorised, and the hydriodic acid formed is titrated with decinormal soda, methyl-orange being used as an indicator.

Sodium sulphite may be estimated in the presence of sodium thiosulphate, by titrating with $\frac{1}{20}$ normal iodine, inasmuch as sodium iodide results from its action on the latter; so that the amount of hydriodic acid formed, titrated as above, is a measure of the sodium sulphite present. W. P. W.

Volumetric Estimation of Sulphides. By F. Weil (*Ber.*, **20**, 695—697).—A reply to Friedheim's criticism (this vol., p. 396) of the author's method for determining hydrogen sulphide in sulphides which are decomposed by hydrochloric or sulphuric acid (Abstr., 1886, 918). Analyses of stibnite were made in the following way: the finely powdered mineral, wrapped in filter-paper, was put into a flask with 50 c.c. of hydrochloric acid, heated in a sand-bath, and the evolved hydrogen sulphide passed into 50 c.c. of a modified Fehling solution, which was diluted with about 100 c.c. of distilled water containing 7 to 8 grams of soda; the filtered solution was made up to 300 c.c., and a portion (25 c.c.) treated with 60 to 70 c.c. of hydro-

chloric acid, and titrated with stannous chloride. The numbers obtained in these analyses were: S = 28·38, 28·18, and 28·59 per cent.
N. H. M.

Manganese in Steel and Iron. By H. C. Babbitt (*Amer. Chem. J.*, **9**, 58—60).—The method is as follows: 5 grams of the sample is dissolved in 50 c.c. of nitric acid (1·20 sp. gr.) and 1 to 2 grams of red lead added together with about an equal bulk of hot water, when it may be boiled for some minutes. After a time, the liquid is decanted, and the residue boiled with fresh portions of hot dilute nitric acid (20 to 25 per cent.) so long as the decanted liquid is coloured by the permanganate formed. The united liquids are filtered through asbestos and the permanganate determined as usual. The presence of lead nitrate does not interfere, and the results obtained are very satisfactory.
H. B.

Decomposition of Chrome Iron Ore. By E. Donath (*Dingl. polyt. J.*, **263**, 245).—The finely pulverised ore is mixed with five times its weight of barium dioxide and heated for half-an-hour in a porcelain crucible over a Bunsen burner. A greenish-yellow mass results, which is completely soluble in cold water acidified with hydrochloric acid. The solution contains the whole of the chromium in the form of chromic acid.
D. B.

Bacteriological Examination of Water. By C. W. Folkard (*Chem. News*, **55**, 124—125).—A bent tube drawn out at one end and of 1 c.c. capacity is adapted by a cotton-wool plug to a test-tube containing the nutrient jelly; the whole being then sterilised. The sealed capillary end of the bent tube is then passed through a hole in the wall of an india-rubber tube through which the water to be examined is running under slight pressure, the point is broken, and as soon as the bent tube is filled, it is withdrawn, the point sealed in a flame and the water transferred to the test-tube by shaking.
A. J. G.

Determination of Organic Carbon and Nitrogen in Waters. By C. A. Burghardt (*Chem. News*, **55**, 121—123).—250 c.c. of the water is mixed with 100 c.c. of a standarised solution containing about 10 grams of chromic acid per litre, and 10 c.c. of strong sulphuric acid. The mixture is boiled for ½ hour, diluted to 1000 c.c., and the excess of chromic acid titrated in 100 c.c. by means of standard ferrous sulphate solution; from these data, the carbon is calculated. For the nitrogen determination, part of the oxidised solution is treated with soda and distilled, the ammonia being collected in a receiver containing acidified water. The method, although only in a preliminary stage, appears to work well.
D. A. L.

Decolorising Power of Bone-black. By G. Laube (*Arch. Pharm.* [3], **25**, 133).—Good animal charcoal, from which defective pieces have been rejected, is powdered, dried at 110°, and preserved as "normal charcoal." 50—100 grams of caramel (as obtained from liqueur manufacturers) is dissolved in an equal quantity of water, 100 c.c. of alcohol is added, and the volume is made up to a litre;

after standing some days the liquid is filtered and marked "normal colour." 5 grams of the normal charcoal is heated to boiling with 200 c.c. of water; 10 c.c. of the normal colour is added, and after 10 minutes' gentle boiling in a reflux apparatus, the liquid is filtered through a double-folded filter. 200 c.c. of water is now measured off and normal colour is added from a pipette until the tint is the same as that of the filtrate. If, for example, 2·1 c.c. of normal colour is required, the charcoal is equivalent to 10—2·1 c.c. = 7·9 c.c. Any other sample of charcoal can now be compared with the normal charcoal. If a sample indicates 5·5 c.c. of the normal colour, its decolorising power in comparison with the normal charcoal will be 70 per cent. J. T.

Quantitative Estimation of Wood in Paper. By C. Wurster (*Ber.*, **20**, 808—810).—Inasmuch as crude wood shavings have been introduced into the paper manufacture, and the paper prepared from them turns after some time yellow and then brown, and finally becomes unsightly, an estimation of the proportion of wood present becomes desirable.

Dimethylparaphenylenediamine imparts a magenta coloration to paper containing wood, but no change is produced with paper prepared from linen or cotton fibre. In order to make this change quantitative, the paper to be examined is moistened, tested with the reagent, and the tint given is compared with those of standard papers tinted and arranged according to scale. As then the oxidation of the dimethylparaphenylenediamine to the red dye-stuff is quantitative, these standard papers can be prepared and estimated by some titrated oxidising solution, such as iodine. A few such estimations are given as examples. V. H. V.

Investigation of Acetyl-compounds; New Method for the Analysis of Fats. By R. Benedikt and F. Ulzer (*Monatsh. Chem.*, **8**, 41—48).—The authors use a modification of Köttstofer's process for the determination of the saponification value of fats. The process is carried out by boiling the acetyl-compounds with strong standard alcoholic potash for 15 minutes, the excess of potash is then titrated with standard hydrochloric acid, about half normal. The amount of potash required for the decomposition is expressed as the "saponification-value," that is, the number of milligrams of potassium hydroxide required for the saponification of 1 gram of the acetyl-compound. If the substance under investigation is an acid, a portion of the potash is used up in neutralising the acid; in such cases the "saponification-value" is the sum of the "acid-value" and "acetyl-value." The former must be determined by a separate titration with standard potash. This method is applied to the determination of the molecular weights of the higher fatty alcohols and hydroxy-acids; the substances are first converted into acetyl-derivatives and then saponified as above. The authors have also applied the method to the examination of fats, and state that where the fats principally contain hydroxy-acids, it is possible to identify the acid and in some cases to detect adulterations, both qualitatively and quantitatively. The fat

is first saponified to obtain the fatty acid, and this is then treated as above. G. H. M.

Analysis of Fats. By B. Röse (*Chem. Centr.*, 1887, 234).—In order to avoid the imperfections of the methods of Oudemans (*J. pr. Chem.*, **96**, 407) and Kremel (*Pharm. Centr.*, **5**, 337), for determining acids of the oleic and linoleic series in presence of solid fatty acids, the author has studied the action of lead oxide on mixtures of these acids in ethereal solution. At the boiling point of ether, an excess of lead oxide rapidly neutralises the acids and even partially converts the liquid acids into basic salts, which remain with the insoluble lead stearate and palmitate. The amount of basic salt formed increases with the time. At ordinary temperatures, however, no basic salt is formed, even during a contact of some weeks; whilst the presence of the solid fatty acids does not hinder the complete neutralisation of the oleic acid by the lead oxide. The soluble lead oleate can, therefore, be accurately separated and determined. M. J. S.

Examination of Butter Colours. By H. B. Cornwall (*Chem. News*, **55**, 49).—The solution of fat in ether is shaken with a solution of potash or soda of such dilution as to be only just alkaline when separated from the fatty layer after a few hours. Annatto and saffron may be looked for in this extract. With sulphuric acid, annatto strikes first a blue or violet-blue, then a green, and finally brownish or somewhat violet colour. These changes of colour are important, as pure butters have been known to give a green coloration, but always without the preceding blue. Turmeric is easily recognised by the action of the alkaline solution. D. A. L.

Estimation of Uric Acid by Potassium Permanganate. By C. Blarez and G. Denigés (*Compt. rend.*, **104**, 789—790).—If the solution of uric acid is too strong, the action of potassium permanganate varies with the strength of the solution and the proportion of free acid.

If the solution contains not more than 1 gram of uric acid in 8000 c.c. the action of the permanganate is regular and is independent of the degree of dilution and the proportion of free acid. 1 c.c. of decinormal permanganate is equivalent to 0·0074 gram of uric acid. The results are the same in hot solutions as in cold. The quantity of uric acid should not exceed 0·1 gram, and the quantity of free sulphuric acid should be about 3·5 grams. The amount of permanganate required to produce the end reaction with the same volume of water containing the same quantity of free acid should be subtracted. C. H. B.

Volumetric Estimation of Acids in Salts of the Alkaloïds. By P. C. Plugge (*Arch. Pharm.* [3], **25**, 45—59).—By using litmus as indicator, the acids in narcotine, papaverine, and narceïne salts can be directly titrated with standard soda solution, and in this respect these feeble bases differ from the strong opium bases. Equally good results are obtained with phenolphthaleïn as indicator. In

general, the salts of the alkaloïds can be titrated directly with phenolphthaleïn as indicator, excepting the salts of the volatile bases, conine and nicotine. In the cases of brucine, morphine, and thebaïne, however, a red coloration makes its appearance before the end of the reaction, but a little experience surmounts this difficulty. In solutions of alkaloïd salts (excepting those of the feeble bases), the amount of free acid can be determined by titration with litmus, and the total quantity of acid by titrating with phenolphthaleïn. The difference gives the quantity of acid combined with the alkaloïd, and from this the amount of alkaloïd can be calculated. Sundry examples of the application of the foregoing principles are given, in which the purity or otherwise of various compounds is determined. J. T.

Assay of Opium. By — Adrian and E. Gallois (*J. Pharm.* [5], **15**, 193—197).—In 1867, Guilbermond proposed to estimate the morphine in an aliquot part of the extract obtained from the opium. More recently Doux proposed to modify Regnault's process in the same direction. He treats 50 grams of opium with 200 c.c. of alcohol at 70°, and takes 105 c.c. of the filtrate as representing accurately 25 grams of opium. The authors hold that to arrive at accurate and comparable results, it is indispensable to take into account, in every case, the amount of water and of soluble constituents contained in the opium. They consider the opium as being composed of water, material soluble in alcohol at 70°, and insoluble residue. The sample for assay is pounded in a mortar; 5 grams is extracted with 50 c.c. of alcohol at 70°, with which it is kept in contact for 12 hours; the residue is then filtered off, dried, and weighed on a tared filter. The loss gives the amount of water and soluble matter, and the amount contained in the portion taken for the morphine estimation is of course deduced. 50 grams of the sample is placed in a tared and stoppered flask with a wide neck, treated with 200 grams of alcohol at 70°, placed in a bath of 25—30°, and frequently agitated. When the estimation of water and soluble constituents is finished, the flask is carefully weighed, and alcohol is added to make up the liquid contents of the flask exactly to 250 grams. After filtering, 200 grams of this liquid exactly contain the morphine from 40 grams of opium; this morphine is precipitated by ammonia, washed with alcohol at 40°, dried, treated with chloroform, and dried again as in Regnault's process, but taking care to wait 36 hours before collecting the deposit. The method requires somewhat more time than Regnault's, but it has the advantage of being applicable to all opiums whatever their composition, and it gives exact results. J. T.

Estimation of Morphine in Opium and its Preparations. By O. Schlickum (*Arch. Pharm.* [3], **25**, 13—32).—The method recommended is founded on that proposed by Dietrich, and depends on the fact that if a not too concentrated solution of morphine salts is mixed with a slight excess of ammonia and half its weight of alcohol, and is boiled down to one-half the volume of the mixture, no precipitation of morphine follows when the original volume of solution is made up by adding water. The perfectly neutral solution thus

obtained remains quite clear and free from morphine crystals. For opium, 3 grams is frequently shaken with a mixture of 15 grams dilute alcohol and 15 grams water and digested during 12 hours. The filtrate is made faintly alkaline with ammonia, and evaporated to half its volume. The solution is made up to its original weight and filtered. 21·25 grams of this filtrate is treated with 5 grams of ether and 0·4 of gram ammonia, and shaken round occasionally during five or six hours. The ethereal layer is taken off with a pipette and passed through two equal filters, on which the morphine is collected and washed twice with 2 c.c. of water each time. After drying at 100°, the morphine is weighed, one paper serving as tare. Of opium extract, 1·5 grams is treated with 10·5 grams of dilute alcohol, and 10·5 grams of water without heat, and filtered. The weighed filtrate rendered slightly alkaline by ammonia is boiled down to one-half, made up to its original weight with water, and filtered. 15 grams of the filtrate is treated with ether and ammonia as above. Of *Tinctura opii simplex* or *crocata*, 25 grams is taken, made slightly alkaline with ammonia, and treated as above. J. T.

Estimation of Cinchonidine in Quinine Sulphate. By L. Schäfer (*Arch. Pharm.* [3], **25**, 64—72).—After reviewing several methods, the author gives one for estimating 1 per cent. or less of cinchonidine in quinine sulphate, based on the extremely slight solubility of quinine oxalate in water in presence of a small excess of potassium oxalate, and the relatively easy solubility of cinchonidine oxalate in such a solution. 2 grams of quinine sulphate is dissolved in a small tared flask in 55 c.c. of boiling water, and 0·5 gram of neutral, crystallised potassium oxalate in 5 c.c. of water is added. The liquid is made up to 625 grams and cooled for half an hour in water at 20°, with occasional shaking to and fro, and then filtered If on the addition of one drop of officinal aqueous soda to the filtrate no turbidity appears, the quinine sulphate contains less than 1 per cent. of cinchonidine sulphate. In the presence of 1 per cent. of the latter salt, a turbidity or a precipitate of cinchonidine appears. Quantitatively, 5 grams of quinine sulphate is taken, and an aliquot part of the filtrate is treated with aqueous soda; the cinchonidine is collected. Since a certain amount of cinchonidine remains in solution, and a little also goes down with the quinine oxalate, it is necessary to apply a slight correction to the amount found. Numerous experiments show that this correction should be 0·04 gram cinchonidine for each 100 c.c. of solution originally taken. Further, if more than 4 per cent. of cinchonidine is present, a more dilute solution should be employed, as the process is expressly intended for small quantities only. The test also indicates small quantities of quinidine and cinchonine sulphate when present; indeed, the conditions are more favourable in the case of these compounds, as they are not carried down by the oxalate precipitate. J. T.

Testing Quinine Sulphate. By O. Schlickum (*Arch. Pharm.* [3], **25**, 128—129).—Employing De Vrij's chromate method (this vol., p. 404), the author finds that not only quinine but also cinchonine

forms a chromate soluble in 2000 parts of water at moderate temperatures, whilst quinidine and cinchonidine chromates are much more soluble in water. On precipitating a quinine solution by means of normal potassium chromate, and allowing it to remain four or more hours, the filtrate remains unchanged on the addition of soda if the quinine salt is pure. If the quinine salt contains cinchonine, quinidine, or cinchonidine in not too minute traces, the soda produces a turbidity either at once or after some time. The method detects cinchonine sulphate to $\frac{1}{2}$ per cent., and cinchonidine or quinidine sulphate to 1 per cent. In testing other neutral quinine salts it is not necessary to convert them into sulphate. Acid quinine salts require conversion into neutral ones, say by evaporation to dryness with ammonia. J. T.

Colour Reactions of Picric Acid and Dinitrocresol (Victoria-yellow). By H. Fleck (*Chem. Centr.*, 1887, 99).—When solutions of these substances are evaporated in a porcelain dish, and the residue moistened with a little 10 per cent. hydrochloric acid, a small piece of pure zinc added, and the dish allowed to remain for some hours without warming, a fine blue colour is developed in the case of picric acid and a bright blood-red with dinitrocresol. These reactions are useful for examining artificially-coloured farinaceous foods, the alcoholic extract of which should be employed. G. H. M.

Determination of Tannin in Sumach. By J. Macagno (*Chem. Centr.*, 1887, 125).—The author has compared Löwenthal's method for the determination of tannin with those of Davy and Gerland. He finds that Davy's method, which consists in precipitating the tannin with gelatin, drying, and weighing the precipitate, and multiplying the weight by the factor 0·4, gives results both with pure tannin and also with sumach which stand in the ratio to results obtained by Löwenthal's method as 53·34 : 100; whilst Gerland's method (precipitation of the tannin with tartar emetic solution in the presence of ammonium chloride; the reagent is prepared by dissolving 2·611 grams dry tartar emetic in a litre of water, 1 c.c. equals 0·005 gram tannin) gives results which, when compared with Löwenthal's method, stand in the ratio of 2 : 3. G. H. M.

General and Physical Chemistry.

Absorption-spectrum of Liquid Oxygen and of Atmospheric Air. By K. Olszewski (*Monatsh. Chem.*, 8, 73—77).—Liquid oxygen, examined with a thickness of 12 mm. and at a temperature of −181·4°, gives absorption-bands, the middle of which correspond with the wave-lengths 628, 577, 535, and 480μ; the band 628 is characterised by its width (634—622), and the band 577 by its intensity: the bands 535 and 480 do not appear to be present in the solar spectrum.

Liquid air was examined at −191°, and with a thickness of 12 mm. No other absorption-bands besides those of oxygen were observed, but bands 628 and 577 were not so strong as with pure oxygen.

G. H. M.

Red Fluorescence of Alumina. By L. de Boisbaudran (*Compt. rend.*, **104**, 824—826).—The author has previously found (this vol., p. 538) that alumina prepared from pure aluminium chloride shows no phosphorescence even in the phosphoroscope. An aqueous solution of the chloride was left exposed to the air in a glass vessel for several days, and was then evaporated to dryness, and the residue strongly heated. The alumina thus obtained gave no fluorescence in a vacuum, and only a very feeble tint in the phosphoroscope.

Alumina from aluminium chloride, which has been very strongly heated and shows no phosphorescence in the phosphoroscope, shows a brilliant red phosphorescence when mixed with a very small quantity of chromium.

In order to ascertain whether the fluorescence shown by alumina from alum is due to the presence of impurities, ammonia alum was recrystallised seven times from a slightly acid solution. Alumina prepared from the seventh crystallisation, and very strongly heated, gave no red fluorescence in a vacuum, but a moderately intense violet fluorescence, becoming indigo with a weaker current. In the phosphoroscope, it showed a very feeble greenish phosphorescence with a tendency to become red at some points. Alumina from the fifth crystallisation gave no red in a vacuum, but a somewhat marked pale green fluorescence, becoming violet with a weaker current. The alumina from the third crystallisation gave the red fluorescence, and the mother-liquor gave the spark spectrum of chromium.

Alumina precipitated from the seventh crystallisation by ammonia, and very strongly heated, showed no trace of the red fluorescence in a vacuum, but gave a mixture of a feeble green and a still feebler violet fluorescence. If this alumina is mixed with 0·0000186 of its weight of chromium oxide, it shows a beautiful rose-red fluorescence.

The author considers that these facts, together with those previously described, show that the red fluorescence is really due to the presence of minute quantities of chromium.

C. H. B.

Molecular Refraction of Carbon Compounds of High Dispersive Power. By R. Nasini (*Gazzetta*, **17**, 48—55, and 55—64).—In these papers the author criticises Brühl's conclusions regarding the relations between molecular refraction and chemical constitution. The papers are mainly controversial, and contain neither fresh determinations nor conclusions. V. H. V.

Formation of the Electric Arc without Contact of the Electrodes. By G. Maneuvrier (*Compt. rend.*, **104**, 967—969).—The electrodes are enclosed in an air-tight glass vessel provided with a three-way stopcock, the electrodes being connected with a source of alternating currents by means of platinum wires fused into the glass. The apparatus is attached to an air-pump, and the pressure inside reduced until a violet silent discharge takes place between the poles. The stopcock is then turned so as to admit a small quantity of air, and under the influence of the sudden increase of pressure, the silent discharge between the poles is transformed into an arc. When the arc has formed, the stopcock is closed, and in this way an arc is obtained in what is practically a vacuum, and thus many of the causes which interfere with the constancy of the arc are eliminated; there is, for example, no combustion of the carbons. The silent discharge passes when the pressure in the globe is 5—6 mm., and the arc is formed at pressures between 30 and 150 mm. C. H. B.

Thermic Expansion of Liquids at Various Pressures. By G. P. Grimaldi (*Gazzetta*, **17**, 18—31).—In continuation of experiments on the expansion of liquids at various pressures (Abstr., 1886, 498), the author gives determinations for chloroform at temperatures varying from 0—80° and pressures of 1 to 15·5 metres, and of pentane between 1 and 100°, and pressures of 1 to 22 metres. The equation expressing the expansion in terms of temperature is of the form $\Delta = at + bt^2 + ct^3$, and the values for the constants a, b, c are given for chloroform and pentane at pressures of 1 and 15·5 metres and 12 and 22 metres respectively.

The various formulæ, expressing the dilatation in terms both of temperature and pressure, which have been proposed by Duprè, Heen, and van der Waals are fully discussed. The formula most in accordance with the results is a modification of Dupré's, and is expressed thus: $K = \frac{T\alpha V}{\beta}$, in which $K = \alpha\Delta^2$ when $t = 0°$, T is the absolute temperature, α the time coefficient of dilatation at pressure p, β the coefficient of compressibility at T, and K a constant dependent on the nature of the liquid examined. The difference between the observed and calculated values is most marked at the extreme limits of temperature, at which the determinations are least exact, and it is noted that a small error in the experimental value for the expansion influences to a considerable degree the value for the constants α and β. The coefficients calculated according to Heen's equation give results lower than those observed, and these differences rapidly increase with increase of temperature. V. H. V.

Latent Heat of Vaporisation of Certain Volatile Substances. By J. Chappuis (*Compt. rend.*, **104**, 897—900).—The apparatus consists of a cylindrical glass reservoir closed at the bottom, and containing the liquid to be evaporated. This receiver terminates in a serpentine capillary tube united to an ordinary delivery tube, and to the free end of this a steel stopcock with a lateral tubulus is cemented.

The receiver containing the liquid under examination is weighed and placed in a Bunsen's ice-calorimeter, in which both it and the serpentine tube are completely surrounded by mercury. The stopcock is then opened, and the vapour is allowed to escape very slowly so that the reduction of pressure which is essential to vaporisation may be kept as small as possible. After the usual readings have been made, the apparatus is again weighed. The loss of weight gives the difference between the weight of the liquid which has been volatilised and the weight of its saturated vapour which occupies the same volume; from this, the weight of the liquid evaporated is readily calculated. The following results were obtained:—

Methyl chloride.....	96·9
Sulphurous anhydride	91·7
Cyanogen	103·7

Further experiments, which will be described in a subsequent paper, show that the rate of vaporisation exerts considerable influence on the results, but if it does not exceed 8 to 16 mgrms. per minute, the latent heat of vaporisation is constant. Within the same limits, the temperature of the apparatus in which evaporation takes place is not reduced below 0·3°. C. H. B.

The Calorimetric Bomb. By Berthelot and Recoura (*Compt. rend.*, **104**, 875—880).—The calorimetric bomb (Abstr., 1886, 756) consists of three metals, platinum (interior), steel, and brass (stopcock). Its water value may be calculated from the weight of these metals and their specific heats, or may be directly determined by one of three methods, namely: (1) by burning in the bomb in the calorimeter two different weights of the same substance, one being twice or three times as great as the other; the thermometric measurements give equations which contain the value of the unknown quantity; (2) by introducing into the water of the calorimeter containing the bomb a known quantity of water at a definite temperature; (3) by introducing into the water of the calorimeter a known weight of concentrated sulphuric acid, a previous experiment being made with the same quantity of water and sulphuric acid, but without the bomb in the calorimeter. Direct determination gave 343·9 grams; whilst the calculated water value was 344·7 grams.

Ten minutes after compressing the gas, or allowing it to escape, the rate of cooling of the apparatus resumes its normal value. The compressed oxygen from the pump is passed through a copper tube heated to redness in order to oxidise any organic matter, and is cooled to the ordinary temperature before entering the bomb.

Three of these bombs are in existence, and a comparison of the heat

of combustion of naphthalene made by means of the bombs in three separate laboratories, will give some idea of the accuracy of the method—

	Per gram.
Berthelot and Vieille	9·718
Louguinine	9·763
Recoura	9·664
	9·715

The variations only amount to 0·5 per cent., and with greater experience in the manipulation of the apparatus still greater accuracy will be attained. C. H. B.

Dependence of Chemical Affinity on Temperature. By W. Müller-Erzbach (*Ber.*, **20**, 1152—1153).—If t_1 and t_2 be the temperatures at which a hydrated compound and pure water respectively exert the same vapour-tension, the author speculates that $t_1 - t_2$ may be a measure of the firmness of union of the chemically combined water. For all solid hydrated salts hitherto examined, $t_1 - t_2$ diminishes with rise of temperature; but for aqueous solutions of these salts it increases slightly with the temperature (Wüllner, Tamman) up to 100°. For dilute sulphuric acid also, $t_1 - t_2$, calculated from Regnault's experiments, increases regularly with the temperature, but more rapidly for the stronger acids.

Hence the author concluded that, for example, hydrated cupric sulphate and dilute sulphuric acid, enclosed in the same space, could be in equilibrium as regards affinity for water, only at some definite temperature. And, in fact, when the hydrate $CuSO_4 + 3$ to $4\frac{1}{2}$ H_2O and sulphuric acid of 1·418 sp. gr. are enclosed in the same vessel, but not in direct contact, the weight of the copper salt increases in the course of a day at 12°, but at 50° it diminishes perceptibly in a few hours. With acid of 1·427 sp. gr., the changes are of the same kind, but slower, and the action is reversed at about 32°. Below this, the affinity of the copper salt for water is the more powerful, above it that of the acid prevails. Further experiments are promised.

Ch. B.

Thermal Study of Solutions of Hydrobromic Acid, and of the Solid Hydrate, $HBr,2H_2O$. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **5**, 323—334. See Abstr., 1886, 117 and 414). The following are the specific heats, C, of solutions containing n molecules of water to one HBr.

n.	C.	*n*.	C.	*n*.	C.
∞	1·0000	7·01	0·5397	2·92	0·3742
200	0·9688	5·69	0·5005	2·72	0·3608
100	0·9402	4·92	0·4711	2·48	0·3524
50	0·8876	4·85	0·4694	2·0	0·3553
20·12	0·7641	4·65	0·4640	1·84	0·3827
10	0·6154	4·013	0·4310	—	—

The molecular heats calculated from this table are almost identical with the values found by Marignac and Thomsen for solutions of hydrochloric acid. The specific heat and the molecular heat for HBr,nH_2O reach minimum values for $n = 2$. When the molecular heat is calculated for $n'HBr,100H_2O$, the value is a minimum for $n' = 8$. These results do not point to the hydrates of HCl and HBr, supposed to exist by Berthelot (*Ann. Chim. Phys.* [5], **4**, 488). The author rather supposes the solutions to contain several molecular groupings in dynamical equilibrium, the composition and quantity of these groupings varying with the temperature and concentration. Similar views as to the constitution of solutions of sulphuric acid are held by Mendeléeff (Abstr., 1886, 413).

The author has also determined the heat of dilution of the *liquid* hydrate, $HBr,2H_2O$, and finds it = 5880 cal. at 10°. Its value increases with the temperature by about 40 cal. for 1°. The heat of solution of the *solid* hydrate, $HBr,2H_2O$, at −15·5°, when dissolved in about 150 mols. of water at 10°, = 1778 cal. The difference between this and the heat of dilution of the liquid hydrate at the same temperature gives heat of fusion of $HBr,2H_2O$ = 3045 cal. Finally, heat of formation of solid $HBr,2H_2O$ at −15° = 1692 cal.

By means of these tables, the *heat of transformation* of the solid hydrate, that is, the heat necessary to convert 1 mol. of hydrate partly into solution, partly into gas, or into solution of greater concentration, may be calculated. These numbers are extensively used in the following papers. Ch. B.

Conditions of Equilibrium of Two Substances in the Three States, Solid, Liquid, and Gaseous. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **5**, 335—350).—The following investigation is due to van der Waals. Gibb's thermodynamic equation $dp/dt = dy/dv$ (y = entropy) or $Tdp/dt = Q/dv$, for a system of $n + 1$ coexistent phases of n substances, may be applied to the case of the solid hydrate of a gas, in presence of a solution and of the free gas. Q may be expressed as the heat of transformation (see last Abstract) of a molecule of the solid hydrate, $H_2O + c$ mols. gas, into a solution $H_2O + x$ mols. gas, and $c - x$ mols. gas; and d/v as the increase of volume due to this transformation. The curve dp/dt (t = abscissæ, p = ordinates) is then the curve of equilibrium for the three coexistent phases. It is shown, that when $c > x$, Q and dp/dt are positive; when $c = x$, dp/dt is either very great or infinite; when $c < x$, either Q = + and dp/dt = −, or Q = − and dp/dt = +.

The curves (p, t) for different concentrations (x) of the coexistent solution may be similarly calculated. In this case, Q = heat necessary to expel 1 mol. of gas from a solution of supposed constant composition. The values $dp/dt - (\delta p/\delta t)_x$ indicate the relative directions of the curve of equilibrium, and the curves (x). These values necessarily have the same sign as dx/dt. An expression for dx/dt involving $(\delta x/\delta p)_T$, heat of fusion, and heat of dilution = Q diss. of the hydrate, and $(c - x)$ is then arrived at, and it is shown that dx/dt is $+ \infty -$, accordingly as $c > = < x$.

From the combined results, three branches of the curve of equilibrium may be distinguished, for which the following relations hold.

1. $c>x$. Q = +, dp/dt = + : Q diss. = +, dx/dt = +.
2. $c<x$. Q = +, dp/dt = − : Q diss. = +, dx/dt = −.
3. $c<x$. Q = −, dp/dt = + : Q diss. = +, dx/dt = −,

and for the points of transition between the branches,

1 and 2. $c = x$. Q = Q fus., $dp/dt = \infty$: Q diss. = Q fus., $dx/dt = \infty$

2 and 3. $c<x$. Q = 0, $dp/dt = 0$: Q diss. = +, dx/dt = −.

The first point of transition represents the highest temperature, the second, the highest pressure at which the three phases can coexist.

The author then constructs a typical curve of equilibrium for the three coexistent phases of two substances. CH. B.

The Hydrate $HBr,2H_2O$. By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, **5**, 351—362).—The author discusses the experimental results already obtained (Abstracts, 1886, 117 and 414) in connection with van der Waals' formula. The curve of equilibrium, constructed from direct observation, consists of three branches, for the first of which dp/dt is positive, for the second negative, and for the third again positive. For the two lowest branches, the agreement with theory is very satisfactory, as the author shows by calculating $\frac{dp}{p}/dt = \frac{d \log p}{dt}$ for different points. The third or upper branch cannot, however, be the continuation of the curve of equilibrium for $HBr,2H_2O$; for although dp/dt is here positive, as theory requires (see last Abstract), dx/dt is also positive, whereas it should be negative; and again, Q should here be negative, whereas the thermal data (last Abstract but one) show that it is positive. Although, then, along this part of the experimental curve a solid hydrate still exists, this cannot be $HBr,2H_2O$. The experimental results are, however, explicable by assuming a hydrate to be formed at high pressures, richer in HBr than the coexistent liquid, whereby a new system is introduced. The author's experiments (next Abstract) have confirmed this prediction in a remarkable way.

When the pressure is such that the gas can be removed, the number of phases is reduced to two; and in the simplest case, when the hydrate has the same composition as the solution, the transformation of the hydrate is perfectly analogous to the fusion of a simple substance. Accordingly $dt/dp = Tdv/Q$ expresses the rise of melting point with pressure. Putting dp = 1 atmosphere, and Q = heat of fusion of one equivalent in kilograms of the hydrate, in gravitation measure, dv = difference in cubic metres of the volumes of the solid and melted hydrate (Tables, *Rec. Trav. Chim.*, **3**, 344), and T = 261·7° = melting point of hydrate under 3/4 atm. pressure, dt = 0·0135°. Experimenting at pressures up to 200 atmospheres, the author finds dt = 0·012, 0·013, 0·016.

The author then shows how the change of melting point may be calculated, when the concentration of the solid and coexistent liquid

are different, Q and *dv* being differently expressed. Interesting geometrical relations are traced between the curves of fusion, the curve of equilibrium, &c. CH. B.

New Hydrate of Hydrobromic Acid, HBr,H_2O. By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, **5**, 363—379).—When the hydrate $HBr,2H_2O$ in contact with gaseous HBr is submitted to pressure, no absorption of gas takes place so long as the temperature is below $-15{\cdot}5°$, whatever be the pressure. Above $-15{\cdot}5°$, fusion of the hydrate and absorption of gas take place as already described. At $-14°$, the hydrate may be completely fused under a pressure of two atmospheres. Absorption of gas by the liquid then continues up to a pressure of three atmospheres, when the new solid hydrate HBr,H_2O appears. Any attempt to increase the pressure beyond this point increases the amount of the solid.

For higher temperatures, the relations of pressure, temperature, and concentration of the coexistent liquid are those of the third branch of the curve of equilibrium attributed to $HBr,2H_2O$ (last Abstracts and 1886, 117 and 414). Tables are now given showing the conditions of equilibrium for this hydrate in contact with a solution down to $-18°$, and for the hydrate both alone and in contact with solid $HBr,2H_2O$ and gas, down to $-28°$. Since the tension of the new hydrate at $-30°$ is less than one atmosphere, the author has been able to collect it for analysis, at this temperature.

The application of van der Waals' theory to the curves of equilibrium of this compound is also discussed. CH. B.

Combinations of Ammonium Bromide with Ammonia. By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, **5**, 387—392).—The author discusses the curves of equilibrium of the compounds NH_4Br,NH_3 and $NH_4Br,3NH_3$, in contact with ammonia (Abstr., 1886, 500), in connection with van der Waals' theory. These compounds are strictly analogous to the hydrates $HBr,2H_2O$ and HBr,H_2O (previous Abstracts). No new experimental results are given. In the first paper, the equilibrium curves are incorrectly spoken of as curves of tension of the solid and liquid compounds. CH. B.

Influence of Concentration on the Vapour-tension of Ethereal Solutions. By F. M. RAOULT (*Compt. rend.*, **104**, 976—978).—For concentrated solutions, D, the diminution of vapour-tension resulting from the solution of 1 mol. of the substance in 100 mols. of ether, ceases to be constant (this vol., p. 207), and diminishes as the quantity of dissolved matter increases, finally becoming *nil*.

If $y = D \times 10000$ and $x =$ the number of molecules of the substance dissolved in 100 mols. of ether, and curves are constructed having the values of y for ordinates and the values of x for abscissæ, it is found that the curves representing the behaviour of different substances are of the same general character, and coincide more or less completely at their extremities, and in some cases even throughout their whole length. A mean curve can therefore be readily con-

structed, and the first part of this curve, which includes the values of x between 10 and 100, is represented by the equation—

$$y = 100 - 1{\cdot}105x + 0{\cdot}0053x^2,$$

whilst the second part, comprising the values of x from 100 to 700, is given by the expression—

$$y^3x^2 = 760000000.$$

The differences between the observed and calculated values vary with the nature of the substance, but never exceed one-thirtieth, and are frequently much less. When the value of x is very large, the differences disappear, and the two equations furnish simple laws sufficiently exact to be of value for the determination of molecular weights.

There is evidence that other liquids which act as solvents behave in a manner analogous to ether. C. H. B.

Apparatus for Determining Vapour-densities. By W. Bott and D. S. Macnair (*Ber.*, **20**, 916—922).—The apparatus is similar in principle to that described by Dyson (this vol., p. 431), and in addition results obtained by its use are given which agree well with the numbers required by theory. A simple device is also described by which the movement of a piece of soft iron suspended by two thin platinum wires, when attracted by a magnet outside, is made to bring about the fall of the experimental bulb into the hot chamber of the apparatus. W. P. W.

Variation of Solubility with Variations in the Heat of Solution. By G. Chancel and F. Parmentier (*Compt. rend.*, **104**, 881—882).—A reply to Le Chatelier (this vol., p. 548).

Effect of Nitric Acid on the Solubility of Nitrates. By R. Engel (*Compt. rend.*, **104**, 911—913).—Each molecule of nitric acid up to about the thirtieth precipitates practically 1 mol. of sodium nitrate, a result identical with that obtained with hydrochloric acid and the chloride. At first, the sum of the molecules is somewhat higher and afterwards somewhat lower than it should be if the law were absolutely true.

Whilst the quantity of acid added is small, the action remains purely physical, and the amount of salt precipitated is proportional to the quantity of acid added. According to Van t'Hoff, equilibrium under these conditions results from equality of the osmotic forces of the liquids. The numbers calculated on this assumption are practically identical with the numbers actually observed, and since the same law holds good in the case of the chlorides, it is highly probable that a simple relation exists between the osmotic forces of saturated solutions of metallic chlorides, and consequently between their vapour-tensions.

When the proportion of acid becomes large, chemical action intervenes, and soon predominates over the physical action. This change consists of the formation of acid salts. The acid nitrates of potas-

sium and ammonium have been isolated by Ditte. Nitric acid at first precipitates ammonium nitrate from its solution molecule for molecule, then a minimum of solubility is passed, and afterwards the solubility increases with the amount of acid. In the case of potassium nitrate, the minimum of solubility is very quickly passed, and the influence of the chemical change is in fact perceptible at the outset.

C. H. B.

Critical Remarks on the Avidity Formula. By G. A. Hagemann (*Ber.*, **20**, 556—562).—Thomsen's theory of the avidity of acids (*Thermochemische Untersüchungen*, **1**) has been apparently confirmed by Ostwald's investigations (*Ann. Chem. Phys. Ergb.*, **8**, 154, and **2**, 429). The author points out, however, that Thomsen is inconsistent in regarding the solution in water of such substances as Na_2O and SO_3 as purely physical phenomena, and yet introducing the attendant heat changes into the calculation of a chemical constant. Ostwald, who has studied the volume changes attending the mixture of an acid and a base, entirely neglects the influence of the water of solution; and the author shows that when this latter is taken into account the expression for the phenomenon is not simply (Na_2OAq,SO_3Aq), but is much more complex.

Every such reaction is in fact a double decomposition, and it is doubtful if Berthollet's problem was correctly stated, since the influence of the solvent water must always enter into it. In the author's opinion, however, although the calculations of "avidity" are entirely false, the agreement between Ostwald's and Thomsen's results is important as confirming his theory of the residual energy, basic or acid, of neutral salts (*Studien über das Molecular-volumen einiger Körper*). This theory has been strengthened by the experiments of Trey (this vol., p. 102), who has shown that haloïd salts in general accelerate the catalytic decomposition of methyl acetate by hydrochloric acid, their residual energy being acid, while sulphates in general retard it, their residual energy being basic. Solutions of acids, bases, and salts, are in reality chemical combinations in indefinite proportions.

Ch. B.

Hagemann's Critical Remarks on the Avidity Formula. By J. Thomsen (*Ber.*, **20**, 1155—1157).—According to the author Hagemann in his criticisms (preceding Abstract) confuses positive changes of volume and contractions, or negative changes.

Electrolysis of Hydrochloric Acid; a Lecture Experiment. By M. Rosenfeld (*Ber.*, **20**, 1154—1155).—In this paper, an apparatus is described to illustrate the electrolytic decomposition of hydrochloric acid, and the formation of a detonating mixture of hydrogen and chlorine. It consists of two concentric cylinders, the outer one of which serves for a steam jacket, and in the inner one is placed a mixture in equal volumes of hydrochloric acid and water, which has previously been saturated, when hot, with sodium chloride. This solution is electrolysed by two carbon poles connected with a battery. By the use of this apparatus, an explosive mixture of the two gases is obtained very rapidly.

V. H. V.

Lecture Experiment. By C. Schall (*Ber.*, **20**, 915—916).—The specific heat of zinc is nearly twice as great as that of tin, and this, taken in conjunction with the fact that both metals have nearly the same specific gravity, renders them suitable for demonstrating Dulong and Petit's law for lecture purposes. Rods of the two metals of similar section and equal weight are heated to 150—170°, and then placed on paraffin-wax; the paraffin melted by each can be weighed, and is proportional to the specific heat of the metal in question.

W. P. W.

A Constant Gas Generator. By C. Sleenbuch (*J. pr. Chem.* [2], **35**, 364—368).—The essential part of the apparatus consists of a kind of **U**-tube, the one limb of which is of a shape suitable to contain the marble, zinc, manganese dioxide, &c., the other prolonged and terminating in a bulb. At the base of the **U**-tube, another tube is blown, which is fitted by means of a cork into a Woulff's bottle, and reaches nearly to the bottom of this. In the latter tube, a small side tube is sealed to enable the air in the Woulff's flask to be driven out by the liquid. In this way the spent and heavy acid flows into the Woulff's bottle (and may from time to time be syphoned off by a tube leading from the other neck of the bottle), while the available acid in the pressure tube is always the lighter and fresher acid. By surrounding the limb of the apparatus containing the manganese dioxide, &c., with a coil of metal tubing through which steam is passed, the apparatus may be used as a chlorine generator.

L. T. T.

Inorganic Chemistry.

Amount of Oxygen in the Atmosphere. By U. Kreusler (*Ber.*, **20**, 991—999).—The author has determined the amount of oxygen in the atmosphere for 45 consecutive days, and found only very slight variations, the extremes being 20·901 and 20·939 per cent. (compare *Landwirtschaft Jahrb.*, **14**, 305). Tables are given showing the percentage of oxygen obtained each day, and also the meteorological conditions under which the experiments were made.

N. H. M.

Boiling Point of Ozone: Solidification of Ethylene. By K. Olszewski (*Monatsh. Chem.*, **8**, 69—72).—Ozone was liquefied by passing a current of ozonised oxygen through a tube cooled by liquid oxygen boiling at atmospheric pressure. It liquefies with ease at −181·4° to a dark-blue liquid, whilst the oxygen passes away through the open end of the tube. The boiling point of the liquefied ozone, determined by the aid of liquid ethylene, with a carbon bisulphide thermometer, was found to be −109°; this corresponds with −106° of the hydrogen thermometer. It is necessary to exercise great care in performing the above experiment on account of the readiness with which liquid ozone explodes with violence when it comes in contact with

ethylene gas. A small quantity of liquid ozone sealed up in a glass tube changed, at the ordinary temperature, to a bluish gas.

Former experiments to solidify ethylene were unsuccessful (Abstr., 1885, 1101), but the author has now succeeded in solidifying this gas to a white, crystalline, somewhat transparent mass, by allowing the liquid gas to boil under a pressure of 1 mm. at the boiling point of oxygen (−181·4°). The melting point of the solid ethylene is −169°.

G. H. M.

Reaction of Nitrous Acid with Sulphurous Acid. By F. Raschig (*Ber.*, **20**, 1158—1163).—In a former paper (this vol., p. 549) the author has shown that hydroxylamine reacts with sulphurous acid to form an amido-sulphonic acid. In this preliminary communication, speculations are put forward regarding the possible reactions between free nitrous and sulphurous acids, with especial reference to the chemical changes which occur in the leaden chambers of the sulphuric acid manufacture. These speculations are not here, however, supported by experimental evidence. V. H. V.

Oxidation of Ammonia in Presence of Platinum or Palladium. By K. Kraut (*Ber.*, **20**, 1113—1114).—If in the well-known experiment illustrating the oxidation of ammonia by means of a glowing spiral or foil of platinum, a current of oxygen is passed into the solution of ammonia, a white cloud of ammonium nitrate is at first produced, and subsequently fumes of nitrogen peroxide appear, which increase until an inflammable or even explosive mixture of gas is formed. V. H. V.

Hydroxylated Solid Hydrogen Phosphide. By B. Franke (*J. pr. Chem.* [2], **35**, 341—349).—The so-called oxide of phosphorus is generally looked on as a mixture of phosphorous and phosphoric acids. Le Verrier (*Annalen*, **27**, 167) obtained this substance in greater purity by exposing to the air phosphorus half covered with phosphorous chloride. The aqueous solution of the substance so obtained decomposed at 80° into free phosphoric acid and yellow flocks of a substance which he believed to be a hydrated oxide of phosphorus. The author has obtained the same substance by the action of water on P_4I_2. The iodide is prepared by mixing the required quantities of phosphorus and iodine in carbon bisulphide solution; this solution is then gradually added, with constant agitation, to water. No separation of phosphorus occurs, but the aqueous solution (of $OH{\cdot}P_4H,HI$) becomes of a golden-yellow colour whilst the carbon bisulphide becomes colourless. The aqueous layer is separated and heated to 80°, when it becomes colourless, deposits yellow flocks, and contains now only hydriodic and a little hypophosphorous acids. These flocks have the composition $P_4H{\cdot}OH$. This substance decomposes, slowly under water, more rapidly in moist air, into hypophosphorous acid, phosphorus, and gaseous hydrogen phosphide. The analysis was made by heating strongly in a current of carbonic anhydride. The residue, consisting of amorphous phosphorus and phosphoric anhydride, was weighed, then oxidised with nitric acid, and re-weighed; the gaseous hydrogen phosphide evolved was measured.

This hydroxylated hydrogen phosphide dissolves in alcoholic potash with evolution of hydrogen from the compound to $P_4H{\cdot}OK$, but on adding water to the solution decomposition takes place according to the equation—

$$3P_4H{\cdot}OK + 6H_2O + 3KOH = 6KPH_2O_2 + 2PH_3 + 4P.$$

This substance forms part of the reddish-white coating which gradually covers phosphorus when kept under water.

The author finds that when hydrogen phosphide is acted on by dilute potash it is completely decomposed, probably according to the equations—

$$4PH_3 + 4KOH = 4PH_2{\cdot}OK + 4H_2 = P_4H_2 + 5H_2 + 4KOH.$$

L. T. T.

Hydrates of Potassium Hydroxide. By C. Göttig (*Ber.*, **20**, 1094—1096).—In this paper, two new definite compounds of potash with water are described: of these, one has the composition $2KHO + 9H_2O$, separating from concentrated alcoholic solutions of the alkali (sp. gr. 1·05—1·058) in pyramidal crystals, melting below 40°; when kept over sulphuric acid, it loses 3 mols. H_2O. The second compound, $2KHO + 5H_2O$, is obtained by concentrating alcoholic solutions of potash until a boiling point of 116° is reached; on cooling, the liquid solidifies to a thick magma of interlaced needles. This compound melts below 50°, and when kept over sulphuric acid loses $1\frac{1}{2}$ mols. H_2O, with formation of the hydrate $KHO + H_2O$.

Both the above compounds, when introduced in small quantities into water, exhibit at first a peculiar rotatory motion and then dissolve rapidly. V. H. V.

So-called Argentous Compounds. By W. Muthmann (*Ber.*, **20**, 983—990).—A microscopic examination of the crystals obtained by dissolving silver molybdate, chromate, and tungstate in ammonia to saturation, heating at 90°, and passing hydrogen for some time (Rautenberg, *Annalen*, **114**, 119), shows that they consist of the unaltered salt crystallised with very finely divided metallic silver. Addition of ammonia dissolves the salt and leaves metallic silver undissolved; and if in the foregoing process ammonia is constantly added to replace that removed by the passage of hydrogen through the ammoniacal solution, only finely divided silver is obtained instead of the so-called argentous salts. Silver citrate when heated at 108° decomposes with the formation of metallic silver, and the aqueous solution is not coloured red; when the salt is heated at 100° in hydrogen, argentous citrate and citric acid are not formed as stated by Wöhler and v. Bibra (*Annalen*, **30**, 3), but decomposition-products of citric acid (comp. Trans., 1887, 416) and finely divided silver are obtained together with unaltered salt. The product, contrary to the behaviour of so-called argentous salts, dissolves in ammonia without decomposing into finely divided silver and the corresponding silver salt; the solution is clear, intensely red, and feebly fluorescent, and when largely diluted with water appears transparent and grass-green by transmitted, but opaque and violet by reflected light. The colour of the solution is not due to the presence of argentous salt, but of

finely divided silver; it is instantly destroyed by the addition of acids or salts such as potassium nitrate and sodium sulphate or acetate, and silver is precipitated; shaking with recently ignited animal charcoal removes it, and on dialysis of the solution a deposit of silver is found on the membrane of the dialyser. Addition of gum arabic to the red solution and subsequent precipitation with alcohol removes the colour, and the precipitate gives a red solution with water; moreover, when it is kept at $-12°$ for some hours and the ice formed subsequently melted, a liquid is obtained which is no longer red and transparent, but black and opaque, and deposits finely divided silver on standing. The author concludes, therefore, that argentous salts do not exist.

W. P. W.

Double Phosphates and Arsenates of Strontium and Sodium. By A. Joly (*Compt. rend.*, **104**, 905—908).—The author has previously found (*Compt. rend.*, **103**, 1197) that the reaction between disodium phosphate (1 mol.) and strontium chloride (1 mol.) takes place in three phases. A gelatinous trimetallic phosphate is formed, which then becomes crystalline, and is afterwards transformed into a distrontium phosphate, the neutral solution becoming acid to litmus. If the vessel is free from any crystals formed in a previous operation, the second and third stages can be distinctly separated. The thermometer remains stationary for some minutes, during which the crystalline trimetallic phosphate is isolated. It consists of cubic crystals of strontium sodium phosphate, $NaSrPO_4 + 9H_2O$, almost insoluble in cold water and not decomposed by washing with water.

If the precipitate is allowed to remain in the liquid, and phenolphthaleïn is added and then aqueous soda, a white, gelatinous precipitate is formed which crystallises rapidly. When the indicator changes, one equivalent of alkali has been added, and the whole of the strontium is precipitated as strontium sodium phosphate, which is not affected by water.

When a solution of strontium chloride (1 mol.) is added to a solution of disodium arsenate (1 mol.), no precipitate is formed, and the solution remains alkaline, but after some time, if the sides of the vessel are rubbed, a crystalline precipitate gradually separates, and the liquid becomes acid to litmus but remains neutral to methyl-orange. If the liquid is not agitated, but crystallisation is allowed to take place very slowly, large, cubic crystals are formed and the reaction is complete in 24 hours. The crystals are strontium sodium arsenate, $NaSrAsO_4 + 9H_2O$; the mother-liquor is acid and some of the arsenate remains in solution. If, however, one equivalent of soda is added to the solution, precipitation becomes complete and the precipitate does not alter in contact with water. It likewise undergoes no change even if left in the acid solution.

Similar double salts seemed to be formed with calcium, but in the case of barium the transformation of the precipitate is so rapid that the formation of a double salt cannot be observed. C. H. B.

Ammoniacal Compounds of Cadmium Chloride. By G. André (*Compt. rend.*, **104**, 908—910).—When cadmium chloride is dissolved in well-cooled aqueous ammonia of 20 per cent., and a

current of ammonia gas is passed into the cooled solution, the compound $CdCl_2,5NH_3$ separates in small, anhydrous crystals. Another preparation gave crystals of the composition $CdCl_2,4NH_3 + H_2O$. Both compounds readily decompose. Divers prepared the compound $ZnCl_2,5NH_3 + H_2O$ by a similar method, and some years ago the author obtained the anhydrous compound $ZnBr_2,5NH_3$. When cupric chloride is treated in the same way, it yields the compound $(CuCl_2,5NH_3)_3 + 3H_2O$.

As in Divers's process, the author dissolved the precipitated cadmium compound in ammonia at a gentle heat; when the liquid cooled it deposited large octahedra of the compound $(CdCl_2,3NH_3)_4 + H_2O$, which alter rapidly immediately on removal from the mother-liquor. In presence of water, it is decomposed with formation of a bulky, white precipitate. Other experiments, in which heating was continued for a longer time and the conditions of cooling were somewhat different, gave the compound $(CdCl_2,4NH_3)_2 + H_2O$. When the copper compound is dissolved in ammonia, it recrystallises without alteration on cooling.

The compound $(CdCl_2,2NH_3)_2 + H_2O$, described by Crofts, is readily obtained by adding a saturated solution of cadmium chloride to well-cooled ammonia, and evaporating at a gentle heat. The author also confirms Hauer's statement that when cadmium oxide is boiled for a long time with ammonium chloride it yields the compound $CdCl_2,4NH_4Cl$. Cupric oxide, under the same conditions, yields no double salt; zinc oxide likewise yields no double salt, but forms the compound $(ZnCl_2,2NH_3)_2 + H_2O$. C. H. B.

Ammoniacal Compounds of Cadmium Sulphate and Nitrate. By G. André (*Compt. rend.*, **104**, 987—990).—When a current of ammonia gas is passed into a solution of cadmium sulphate in ammonia, the compound $CdSO_4,4NH_3,2H_2O$ separates as a crystalline precipitate composed of small needles. The same substance is obtained in somewhat larger crystals by dissolving the precipitate in the ammonia at a gentle heat, and allowing the solution to cool. The ratio of cadmium to ammonia is the same as that of copper to ammonia in the corresponding compound, but the cadmium is not completely precipitated. This compound is also obtained by pouring a layer of alcohol on a solution of cadmium sulphate in ammonia. When prepared in this way, it does not lose ammonia so readily as when prepared by the other methods.

Cadmium oxide dissolves somewhat readily in ammonium sulphate, but even after prolonged action the crystals which separate are variable mixtures of ammonium sulphate and cadmium ammonium sulphate. If, however, a solution of ammonium sulphate saturated in the cold is heated with cadmium oxide for several hours, the solution carefully concentrated, and the crystals of ammonium sulphate separated as they form, the compound $CdSO_4,3(NH_4)_2SO_4 + 10H_2O$ is obtained in crystals. Copper oxide and ammonium sulphate under the same conditions yield crystals of ammonium sulphate coloured blue by a small quantity of copper. Zinc oxide treated in the same

way yields crystals of the compound $ZnSO_4(NH_4)_2SO_4 + 7H_2O$, mixed with some ammonium sulphate. The salt obtained by mixing the two sulphates has the same composition.

If cadmium nitrate crystals are added to 20 per cent. ammonia, they at first dissolve rapidly, but the addition of a further quantity produces a bulky, crystalline precipitate which redissolves on gentle heating. When the solution cools, it deposits crystals of the composition $Cd(NO_3)_2,6NH_3 + 2H_2O$; these, when heated, melt with evolution of a little water, and then blacken with a slight explosion. The same substance is obtained in bulky, anhydrous crystals, when ammonia gas is passed into a solution of cadmium nitrate in ammonia. Both the anhydrous and the hydrated salts are decomposed by water with formation of an amorphous, white precipitate. Under similar conditions, copper nitrate yields an analogous compound. The author was unable to obtain the other ammoniacal copper nitrates described by Berzelius and by Kane.

The ammoniacal zinc chloride recently described by Thoms (this vol., p. 551) was prepared by the author three years ago (*Ann. Chim. Phys.* [6], **3**, 84 and 98). C. H. B.

Effect of Manganese and other Substances on the Properties of Steel. By F. Osmond (*Compt. rend.*, **104**, 985—987).—Manganese retards the molecular change of the iron and recalescence during cooling from a high temperature, or in other words keeps the carbon in solution and the iron in the condition β, the effect being greater the greater the proportion of manganese. The same effect is produced by the rapid cooling of non-manganiferous steel, so that the presence of manganese exerts much the same influence as the process of tempering. Tungsten has the same property in a still more marked degree, but chromium seems to produce no similar effect. Silicon has no influence on the effect of the manganese, but sulphur seems to combine with part of the manganese, and thus diminishes its action. Phosphorus has no appreciable effect on the modification of the iron, nor on recalescence.

Every foreign substance in the steel produces its own peculiar effects, but it is to carbon alone that steel owes its characteristic differences from the other forms of iron. C. H. B.

Alkaline Vanadates. By A. Ditte (*Compt. rend.*, **104**, 902—905, and 1061—1064).—When a solution of vanadic anhydride (1 mol.) in a solution of potassium oxide (1 mol.) is evaporated in a vacuum, it deposits slender needles of the salt $2K_2V_2O_6 + 5H_2O$, and the mother-liquor yields white, silky, nacreous needles of the hexahydrate $K_2V_2O_6 + 6H_2O$. If potassium oxide is in excess, the vanadate separates in brilliant, silky, elongated prisms, which only contain 4 mols. H_2O. A solution of vanadic anhydride in an equivalent quantity of potassium carbonate deposits the hydrate $K_2V_2O_6 + 3H_2O$ in stellate groups of needles.

All these hydrates lose their water when heated, and melt to a pale-yellow liquid which solidifies to a white, nacreous mass of the anhydrous vanadate, which has a lamellar fracture. The anhydrous

vanadate is only slightly soluble in water, whilst the hydrates are readily soluble.

A solution of potassium carbonate saturated with an excess of vanadic anhydride at 80° forms a garnet-red liquid, which on cooling deposits the compound $K_2O,2V_2O_5 + 10H_2O$ in orange-red plates. At a higher temperature, the crystals contain $8H_2O$, and have a deeper colour. If the solution is acidified with acetic acid and concentrated at 80°, the salt containing $10H_2O$ is deposited in brilliant, transparent, hexagonal plates, whilst if crystallisation takes place at a higher temperature, the crystals are orange, and contain $3H_2O$. If these crystals are boiled in the mother-liquor they alter as the liquid becomes more concentrated, and form small, deep-red, very brilliant crystals of the anhydrous divanadate $K_2O,2V_2O_5$. When the mother-liquor from a previous crystallisation, containing a certain proportion of potassium acetate, is concentrated by boiling and allowed to cool, it deposits orange-red plates of the composition $2K_2O,3V_2O_5 + 6H_2O$.

When an excess of vanadic anhydride is dissolved in potassium carbonate and mixed with a large quantity of acetic acid, a garnet-red solution is obtained, and if this is heated at 70° it deposits orange crystals of the compound $K_2O,3V_2O_5 + 5H_2O$. If the mother-liquor is filtered off and allowed to cool, transparent, garnet-red crystals of the hydrate $K_2O,3V_2O_5 + 5H_2O$ separate. When heated, all these hydrated acid salts lose their water and melt to a brown liquid, which solidifies to an almost black, crystalline mass, only slightly soluble in water.

If a solution of vanadic anhydride (1 mol.) in water containing rather more than 2 mols. of potassium oxide is filtered and evaporated in a vacuum, it yields colourless, transparent crystals of the salt $2K_2O,V_2O_5 + 4H_2O$, which lose water when heated, then melt, and solidify on cooling to a crystalline mass of the anhydrous salt, $2K_2O,V_2O_5$.

A solution of 3 mols. potassium oxide and 1 mol. of vanadic anhydride, yields very deliquescent, colourless, transparent, channelled crystals of the vanadate $3K_2O,V_2O_5$ with 9 or 12 mols. H_2O, according to the temperature at which crystallisation takes place. It readily forms supersaturated solutions.

A solution of vanadic anhydride containing a large excess of potash deposits no crystals, but if it is agitated with alcohol an oily layer separates, and when this is washed with alcohol it solidifies to a very hygroscopic crystalline mass with a radiating structure. When this is dried on porous plates in a vacuum, it forms brilliant white needles of the composition $4K_2O,V_2O_5 + 20H_2O$; these lose their water when heated, and yield the white anhydrous salt which fuses with difficulty even at a red heat.

The compound Na_2O,V_2O_5, formed when vanadic anhydride (1 mol.) is dissolved in a solution of sodium oxide (1 mol.), crystallises with difficulty, but if a large quantity of the solution is slowly concentrated it deposits translucent nodules consisting of slender, radiating needles of the composition $Na_2O,V_2O_5 + 4H_2O$. If the syrupy solution which will not crystallise is treated with a mixture of alcohol and water, it deposits an oily layer which quickly solidifies and can be

recrystallised from dilute alcohol, when it forms brilliant white, silky needles of the hydrate $Na_2O,V_2O_5,5H_2O$.

When vanadic anhydride is dissolved in a solution of an equivalent quantity of sodium carbonate, the liquid crystallises with difficulty, but when treated with alcohol it yields white needles of the composition $Na_2O,V_2O_5 + 6H_2O$ or $Na_2O,V_2O_5 + 8H_2O$, according to the temperature.

If somewhat more than an equivalent quantity of vanadic anhydride is dissolved in a boiling solution of sodium carbonate, the liquid on cooling deposits a crystalline crust consisting of distinct red transparent crystals of the composition $Na_2O,2V_2O_5 + 5H_2O$. If a solution of the normal vanadate is acidified with acetic acid and concentrated, it yields garnet-red, channelled needles of the composition $Na_2O,2V_2O_5 + 10H_2O$.

The compound $2Na_2O,3V_2O_5 + 18H_2O$ is obtained in friable hexagonal tables, together with the preceding compound, by concentrating an acidified solution of the normal vanadate. It is also obtained in red, prismatic crystals with only $16H_2O$, by dissolving an excess of vanadic anhydride in sodium hydroxide solution, acidifying the cold liquid with acetic acid, and concentrating at about 50°.

A hot solution of soda saturated with excess of vanadic anhydride and concentrated by boiling, deposits brilliant, orange-red plates of the composition $Na_2O,3V_2O_5 + 3H_2O$.

All the hydrated acid salts, when heated, lose water and become deep brown, melt at a higher temperature, and solidify on cooling to a crystalline mass of the very slightly soluble anhydrous salt.

When vanadic anhydride (1 mol.) is dissolved in a solution containing 2 mols. of sodium oxide, filtered, a small quantity of alkali added, and the solution concentrated in a vacuum, it yields colourless, transparent plates of the composition $2Na_2O,V_2O_5 + 18H_2O$. They melt to a colourless liquid which loses water, forming a white substance; this afterwards becomes pale yellow, and is finally converted into the white, very deliquescent, anhydrous salt. If the solution is evaporated to dryness, and the residue extracted with water and alcohol at about 60°, the liquid deposits brilliant needles of the composition $2Na_2O,V_2O_5 + 8H_2O$ on cooling.

If vanadic anhydride is dissolved in a solution of three equivalents of sodium oxide and the liquid slowly concentrated, it deposits bulky colourless, transparent prisms of the disodium salt, and afterwards brilliant white, silky needles of the composition $3Na_2O,V_2O_5 + 26H_2O$. This salt is also often deposited in nodules which contain only $24H_2O$.

When vanadic anhydride is dissolved in a large excess of soda, the solution yields brilliant white needles of the salt $4Na_2O,V_2O_5 + 30H_2O$. If crystallisation takes place in a warm liquid, the crystals contain only $26H_2O$. When the crystals are heated they effloresce, melt in their water of crystallisation, and are finally converted into the very soluble anhydrous salt, which does not melt even at a bright red heat. In this respect, it resembles the corresponding potassium salt.

C. H. B.

Crystallised Niobic Anhydride. By A. Knop (*Zeit. Kryst. Min.*, 12, 610—615).—The author has obtained niobic anhydride in crystals. Borax glass was fused in a platinum crucible, and saturated with niobic anhydride, of which material 30 grams were at his disposal. On cooling slowly, the excess of anhydride crystallised out. It was found that 9·42 per cent. of niobic anhydride was contained in the clear borax glass, and separated out in an amorphous condition when the mass was dissolved in hot water. The larger crystals are in the form of cubes, and appear to belong to the regular system. Their optical properties, however, do not point to the regular system, but show that the crystals must be regarded as rhombic combinations of the three pinacoids, 0P, $\infty\bar{P}\infty$, and $\infty\breve{P}\infty$. All the plane angles are exactly 90°. It is therefore doubtful whether niobic anhydride crystallises in the regular system with optical anomalies, or in the rhombic with a molecular system approaching that of the regular. Ebelmen (this Journal, 1848, 181), who prepared crystallised niobic anhydride from boric acid, was unable to measure the crystals he obtained on account of the small quantity of material at his disposal. He merely stated that they were prismatic. B. H. B.

Ammoniacal Platinum Compounds. By A. Cossa (*Gazzetta*, 17, 1—11).—After reference to the experiments of Reisel, Cleve, and others on ammoniacal platinum compounds, the results of experiments are given on the admixture of solutions of platinic chloride or sodium platinochloride with platosodiamine chloride. At ordinary temperatures, if the solutions are neutral, a yellow, amorphous compound, of the composition and properties of a platosodiamine platinochloride, is produced. This changes slowly at ordinary temperatures, more rapidly on boiling, into platinodiamine platinochloride (Cleve's salt), when the original substances are mixed in equimolecular proportions, or into the green salt of Magnus and platinodiamine chloride if in the original mixture the proportion of platosodiamine chloride predominates. The results of experiments with various mixtures are given in full. It is evident that the platosodiamine platinochloride has the same percentage composition as platinodiamine platinochloride; thus the yellow, amorphous substance may only be a so-called physical isomeride of the red, crystalline salt obtained directly at temperatures above 60°. In order to determine this point, the reaction between the yellow substance and potassium platinochloride is examined; for if the former is platosodiamine platinochloride it should give by double decomposition platosodiamine platinochloride (Magnus' salt) and potassium platinochloride, thus: $Pt(NH_3)_4Cl_2,PtCl_4 + 2KCl,PtCl_2 = Pt(NH_3)_4Cl_2,PtCl_2 + 2KCl,PtCl_4$. This was confirmed by experiment. V. H. V.

Mineralogical Chemistry.

Origin of Hydrogen Chloride, Sulphurous Anhydride, and Iodine in the Gases of Volcanoes. By L. Ricciardi (*Gazzetta*, **16**, 38—42).—Gay-Lussac, Bunsen, and others, who have studied the gaseous emanations from craters and fumaroles, have concluded that at the commencement of the eruption, hydrogen chloride is evolved, which is succeeded immediately by sulphurous anhydride and other compounds. On the other hand, in the case of the eruption of Etna in the year 1883, the author found this order to be reversed, in that sulphurous anhydride was first evolved and subsequently hydrogen chloride; this point, however, is not insisted on.

As regards the origin of the hydrogen chloride, it probably arises from the decomposition of metallic chlorides, especially magnesium chloride, in the presence of steam at a high temperature. In confirmation of this view, it is shown that finely-powdered granite and lava, mixed with pure sodium chloride, evolves hydrogen chloride, the quantity of which is increased by blowing in a current of steam. On repeating the experiment, with the addition of a small quantity of potassium iodide, iodine is evolved, an element which has been found in the gaseous emanations from the crater of the island Vulcano in the Æolian group. Lastly, the formation of sulphurous anhydride is in all probability due to the interaction of calcium and magnesium sulphates, either singly or conjointly with the silica, whereby silicates are produced with separation of sulphuric oxide, which is decomposed into sulphurous oxide and oxygen. Thus (1) $SiO_2 + MgSO_4 = MgSiO_3$ (enstatite) $+ SO_3$; (2) $SiO_2 + CaSO_4 = CaSiO_3$ (wollastonite) $+ SO_3$; and (3) $SiO_2 + CaSO_4 + MgSO_4 = MgCaSiO_4$ (monticellite) $+ 2SO_3$. It was found that an artificial mixture of granite with magnesium or calcium sulphates evolved sulphurous anhydride.

On the other hand, Bunsen attributes the formation of sulphurous anhydride to the oxidation of hydrogen sulphide, as also to the decomposition of sulphates of the alkalis and alkaline earths at high temperatures. V. H. V.

Stromeyerite from Mexico. By G. A. König (*Zeit. Kryst. Min.*, **12**, 621).—An analysis of stromeyerite from Zacatecas in Mexico gave the following results:—

S.	Ag.	Cu.	Insol.	Total.
15·81	50·18	33·69	0·26	99·94

This corresponds with the formula $(AgCu)_2S$. The mineral occurs in imperfect prismatic crystals in quartz. Its sp. gr. is 6·23. B. H. B.

Braunite from Jakobsberg in Wermland. By L. J. Igelström (*Zeit. Kryst. Min.*, **12**, 659—660).—This mineral, discovered by the author some years ago, is found massive or in small crystals in

Archæan limestone. Analyses of the crystals gave the following mean results:—

SiO_2.	MnO.	FeO.	MgO,CaO.	PbO.	O.	Total.
8·67	(80·23)	1·33	0·95	0·65	8·17	100·00

The silica gelatinises with hydrochloric acid. B. H. B.

Buratite from Laurium. By E. Jannettaz (*Zeit. Kryst. Min.*, **12**, 645).—The mineral forms small bundles of pale-green needles. The needles exhibit oblique extinction. Analysis gave the following results:—

CO_2.	CuO.	ZnO.	H_2O.	Residue.	Total.
15·45	18·07	50·45	14·75	0·50	99·22

B. H. B.

Analyses of Bohemian Minerals. By B. Erben (*Zeit. Kryst. Min.*, **12**, 664—666).—The author gives analyses of the following minerals:—1. Carbonates from the felspar-basalt of Kolozruky between Laun and Brüx; 2. Fibrous barytes from Mies; 3. Comptonite from Katzenburg, near Leitzmeritz (formula $RAl_2Si_2O_8 + 2\frac{1}{2}H_2O$); 4. Aluminium and ferric sulphates from Webrschan: (*a.*) white microcrystalline aggregate soluble in water, sp. gr. 1·72; formula $(Al,Fe)_2(SO_4)_3 + 15H_2O$, that is, the composition of keramohalite less $3H_2O$; (*b.*) compact yellow mass, becoming deep red on exposure to moist air, easily soluble in water; sp. gr. 2·038; formula $(Fe,Al)_2(SO_4)_3 + 12H_2O$, that is, the composition of Schrauf's ihleite.

B. H. B.

Cyprusite. By J. Deby (*J. Roy. Mic. Soc.*, **4**, 186—191; *Zeit. Kryst. Min.*, **12**, 616—618).—This mineral was first described by Reinsch (Abstr., 1882, 578). It forms thick veins in a melaphyr or dolerite containing zeolites. The principal locality where it is found is near Kynussa on the right bank of the Balahussa stream. The mineral is usually friable, but sometimes quite hard. Its sp. gr. is 1·8. It is insoluble in water, but soluble in acids, leaving an insoluble residue of 16·90 per cent. An analysis of the soluble portion gave the following results:—

Fe_2O_3.	Al_2O_3.	SO_3.	H_2O.	Total.
49·68	3·89	35·34	11·06	99·97;

from which the author deduces the formula $Al_2S_3O_{12},8Fe_2SO_6 + 18H_2O$. The difference from the composition found by Reinsch is considerable. Under the microscope, the mineral is found to consist of hexagonal tablets, and an optical investigation showed that it belongs to the hexagonal system.

The author observed in several places the efflorescences mentioned by Reinsch. Their composition is as follows:—

Insol. in H_2O.	Cu.	Al_2O_3.	SO_3.	H_2O.	Total.
4·88	0·45	17·70	35·19	39·00	97·22

Iron was found to be absent. The mineral was of a greenish-white

colour, and looked exactly like weathered ferrous sulphate. Its formula is $2Al_2O_3,5SO_3 + 25H_2O$. B. H. B.

Hæmatostibiite, a New Mineral from Örebro. By L. J. Igelström (*Zeit. Kryst. Min.*, **12**, 650—651).—At the Sjögrufvan iron mine, Örebro, Sweden, in fissures in compact tephroite in granulite interstratified in Archæan limestone, there occur barytes, a mineral resembling chondroarsenite, and the new mineral. The latter appears black, but is blood-red and transparent in thin sheets. It is rhombic, and exhibits distinct dichroïsm. Analysis gave the following results:—

Sb_2O_5.	MnO.	FeO.	MgO + CaO.	Total.
37·2	51·7	9·5	1·6	100·0

In composition, the new mineral is very similar to manganostibiite (Abstr., 1886, 25). B. H. B.

Composition of Columbite from Graveggia in Val Vigezzo. By A. Cossa (*Gazzetta*, **17**, 31—37).—Steuever has recently found columbite among the pegmatite minerals of Graveggia. It appears that columbite occurs in three typical forms, namely (i) black crystals of metallic lustre, sp. gr. = 5·67, appearing brownish-red, when pulverised; (ii) more lustrous crystals than the preceding, sp. gr. 5·78; and (iii) crystals covered with a paste of a light green colour. An analysis of a specimen of the first type gave the following results:—

Nb_2O_5 and Ta_2O_5.	FeO.	MnO.	SnO_2.	CaO.	MgO.	Total.
78·52	9·84	8·98	0·23	1·17	trace	98·74

In the course of these analyses, it was observed that Marignac's method for the separation of niobic and tantalic acids, which is based on the difference in solubility of potassium fluotantalate and oxyfluoniobate, although convenient for obtaining the acids in a state of purity, is not applicable to their quantitative separation. According to Marignac, potassium fluotantalate crystallises in the trimetric system, but the author shows by examination of the crystals by polarised light that they belong to the clinohedric form, a view confirmed by an examination of a large sample of the salt from the columbite of Connecticut. V. H. V.

Pectolite from Auchensterry Quarry, Kilsyth. By J. Young (*Zeit. Kryst. Min.*, **12**, 620).—The specimens described are the finest examples ever seen from Western Scotland, where pectolite is of somewhat rare occurrence. The mineral occurs in the form of fine greyish-white needles, with harmotome and a black mineral, probably tourmaline, in thin veins in the dolerite at Kilsyth, north-west of Glasgow. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	H_2O.
52·74	0·67	1·20	1·52	31·86	9·60	2·00

B. H. B.

Manganese-zinc Serpentine from Franklin, New Jersey. By G. A. König (*Zeit. Kryst. Min.*, **12**, 621—622).—The mineral examined was compact, dark brown in colour, translucent at the edges, and had a semi-conchoidal fracture; sp. gr. 2·635. The mean of two analyses gave the following results (I) :—

	SiO_2.	Fe_2O_3.	MnO.	ZnO.	MgO.	H_2O.	Total.
I	42·20	2·80	7·44	3·90	29·24	14·04	99·62
II	41·70	—	6·91	3·10	29·24	14·04	94·99

Analysis II gives the results obtained after subtracting 4·15 per cent. of franklinite. The author regards the mineral as a serpentine in which the magnesium is partially displaced by manganese and zinc. B. H. B.

Biotite. By A. Knop (*Zeit. Kryst. Min.*, **12**, 588—607).—The author gives the following analyses of biotite :—

	I.	II.	III.	IV.	V.	VI.
SiO_2....	37·60	32·83	34·82	36·42	37·90	35·83
TiO_2 ...	1·67	3·30	2·00	3·99	0·21	0·00
Al_2O_3 ...	19·68	18·40	16·91	17·92	18·83	18·82
Cr_2O_3 ...	0·18	—	—	—	—	—
Fe_2O_3 ...	2·29	1·46	4·19	2·83	4·22	2·63
FeO	15·04	19·90	15·96	7·04	15·86	0·00
MnO ...	trace	trace	—	—	0·70	trace
MgO ...	13·24	11·56	13·98	20·52	13·50	28·34
BaO....	—	—	—	—	—	6·84
SrO	—	—	—	—	—	0·47
K_2O....	6·18	7·53	7·48	6·54	6·96	6·27
Na_2O ...	0·71	2·09	2·49	2·60	0·59	1·01
H_2O....	3·42	3·05	1·79	2·50	1·23	0·00
Total ...	100·00	100·12	99·62	100·36	100·00	100·21

I. Biotite from Böstenbach near Petersthal; II. Biotite from Freiersbach; III. Biotite from Easton, Pennsylvania; IV. Biotite from Oberbergen in the Kaiserstuhl; V. Biotite from the Klausenalpe: VI. Barium-biotite from the koppite-limestone of Schelingen in the Kaiserstuhl. These analyses exhibit great constancy in the percentages of alumina and alkalis; whilst the percentages of ferrous oxide and magnesia vary in such a way that their sums remain approximately equal. The mean of the six analyses gives the following oxygen ratio :—

	RO_2	:	R_2O_3	:	RO
as	2·1	:	1	:	1·4

This represents the formula $R''_4R^{vi}_2Si_3O_{13}$. This formula might also be written $R_3Si_3O_9 + RAl_2O_4$; in which case biotite may be regarded as a molecular combination of amphiboloid material with spinell. B. H. B.

Pseudo-biotite. By A. Knop (*Zeit. Kryst. Min.*, **12**, 607—609).—A mineral resembling biotite, occurring in the granular limestone of

Schelingen in the Kaiserstuhl Mountains, was found on analysis to have the following composition:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	MgO.	K_2O.	H_2O.	Total.
35·91	1·15	15·18	10·85	0·89	22·80	2·90	10·77	100·45

Formula: $R_4Al_2Si_4O_{15} + 2H_2O$. This altered biotite is termed by the author *pseudo-biotite*. B. H. B.

Analysis of a Pink Clay. By A. Damour (*Zeit. Kryst. Min.*, **12**, 655).—The argillaceous mineral described by Baret is soluble in dilute hydrochloric acid to the extent of 2·95 per cent. The residue is still of a pink colour. Analysis gave the following results:—

SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	K_2O.	H_2O.	Total.
53·11	21·22	1·04	0·40	2·32	0·79	21·70	100·58

Formula: $Al_4Si_9O_{21},12H_2O$. Sp. gr. 2·70. B. H. B.

Meteoric Iron at Fort Duncan, Texas. By S. Meunier (*Compt. rend.*, **104**, 872—873).—This meteorite, which was discovered in 1882, is surrounded by a dull black crust, formed during its passage through the air. The interior has the colour of tin, with a characteristic silky lustre, and a crystalline fracture which shows cleavage. It contains elongated inclusions of the colour of silver, and darker masses with the colour of tombac. The meteorite has the composition: Iron, 92·02; nickel (with traces of cobalt), 6·10; insoluble matter, 1·80 = 99·92; sp. gr. = 7·699. The insoluble matter consists of prismatic crystals of the variety of schreibersite known as rhabdite. The tombac-coloured inclusions are pyrrhotine, F_7S_8, which is associated with daubréelite. In its composition, sp. gr., and the nature of the inclusions, this meteorite is almost identical with that which fell at Branau, July 14th, 1847. C. H. B.

Examination of Schützenhof-Quelle, Wiesbaden. By H. Fresenius (*J. pr. Chem.* [2], **35**, 237—254).—Yield about 160 litres a minute; temperature, 21st March, 1879, 49·2°; sp. gr. at 10°, 1·004999. The analysis gave in 1000 parts by weight:—NaCl, 5·154046; KCl, 0·157510; LiCl, 0·025228; NH_4Cl, 0·012340; $CaCl_2$, 0·585858; NaBr, 0·002534; NaI, 0·000028; $CaSO_4$, 0·134366; $SrSO_4$, 0·020362; $BaSO_4$, 0·000010; $CaCO_3$, 0·139495; $MgCO_3$, 0·124487; $FeCO_3$, 0·002179; $MnCO_3$, 0·000671; $Ca_3As_2O_8$, 0·000060; $Al_2P_2O_8$, 0·000334; aluminium silicate, 0·000401; SiO_2, 0·050907; total, 6·410816; combined carbonic anhydride, 0·127669; carbonic anhydride free, 0·308144; nitrogen, trace; also traces of rubidium, cæsium, nitric and boric acids, copper, hydrogen sulphide, and organic substances. Of the gases given off at the spring, 38·47 per cent. are absorbed by potash. The water contains no bacteria. The water was led from the spring by enamelled iron pipes, but the water acted on them and the packing of the joints, with evolution of hydrocarbons and hydrogen sulphide, but since these pipes have been replaced by earthenware ones, no change is perceptible in the water as delivered at the baths, &c. H. B.

Analysis of Mineral Waters from Servia. By S. M. Losanitsch (*Ber.*, **20**, 1114—1115).—The table gives the analyses expressed in parts per 1000 of the springs of (I) Wrnjačka banja, (II) Bukowik, (III) Palanka, (1V) Alexinačka banja, (V) Ribarska banja, (VI) Wranjska banja, and (VII) Brestowačka banja :—

	I.	II.	III.	IV.	V.	VI.	VII.
Fixed constituents ...	2·0146	2·3576	1·6120	0·2666	0·3280	1·0488	0·8345
K	0·07984	0·05409	0·05518	0·00640	0·01170	0·0264	0·01402
Na	0·63704	0·79809	0·42511	0·00888	0·1039	0·3309	0·15224
Ca	0·07691	0·12901	0·10283	0·07182	—	0·0160	0·08000
Mg	0·06562	0·01693	0·04108	0·00570	0·0092	0·0100	0·00612
Fe	0·00240	0·00499	0·00960	0·00121	—	0·0007	—
Al_2O_3	0·00105	0·00271	0·00199	0·00279	0·0010	0·0005	0·00140
SiO_2	0·11512	0·12185	0·08983	0·02244	0·0636	0·1135	0·05211
SO_3	—	—	—	0·01236	0·0843	0·3166	0·47787
Cl	0·04260	0·01775	0·03195	0·00570	0·0065	0·0568	0·04970
CO_2	3·61147	4·53046	3·69433	0·28114	0·0956	0·2546	0·03236
SH_2	—	—	—	—	0·0105	—	0·00425
Sp. gr.	1·0031	—	1·00257	1·00043	1·000345	1·001	1·00075
Temperature..	36°	13°	—	46·5°	39°	89°	40°

A. J. G.

Analysis of the Water of a Saline Lake near the Stolüpin Mineral Springs. By P. Bulitsch (*J. pr. Chem.* [2], **35**, 360—363).—The author has analysed the water from a triple lake about 40 miles from Balakowo, Samara. 1000 parts contained in grams 25·855 Cl, 0·009 SiO_2, 0·002 Fe_2O_3, 2·343 SO_3, 1·755 CaO, 2·099 Mg, 4·722 KCl, 28·497 NaCl, 0·019 Br, and total solid residue 45·483. The water was colourless, had an odour of hydrogen sulphide, a bitter saline taste, and a sp. gr. 1·0348 at 18°.

The water was concentrated till it attained a sp. gr. of 1·21 at 18°, during which process calcium sulphate crystallised out. The mother-liquor had a yellowish colour, and slightly acid reaction. 1000 parts contained in grams 160·575 Cl, 0·025 SiO_2, 1·399 SO_3, 11·908 CaO, 11·200 Mg, 17·617 KCl, 174·244 NaCl, 0·793 Br, and a total residue of 262·606 grams. L. T. T.

Organic Chemistry.

The Relation between Petroleum and the Hydrocarbons of Coal-tar and Shale-tar. By G. Kraemer and W. Böttcher (*Ber.*, **20**, 595—609).—The results arrived at by the authors in an examina-

tion of German petroleum combined with those obtained by Markownikoff in the case of Baku oil (Abstr., 1884, 1276) are held to prove that the hydrocarbons of petroleum and those present in coal- and shale-tar differ, not in character, but in the relative proportions of the two classes of hydrocarbons: those unattacked and those attacked by concentrated sulphuric or nitric acids. To the first group belong the paraffins and naphthenes, and to the second benzene- and, according to the authors' views, naphthene-derivatives. W. P. W.

New Class of Ferrocyanides and Ferricyanides. By J. A. Muller (*Compt. rend.*, **104**, 994—996).—The formation of a violet precipitate on adding ferric chloride to certain solutions of ferri- or ferro-cyanides has been observed by Ortlieb and by Schützenberger, but the substance was not examined.

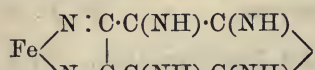
The author has obtained a considerable quantity of this violet substance, and has submitted it to investigation. The substance was treated with a warm solution of potassium carbonate insufficient for complete decomposition, filtered, the filtrate made alkaline with potash, boiled, again filtered, concentrated to saturation, and mixed with alcohol to precipitate potassium ferrocyanide. The last filtrate when carefully concentrated yields thin scales and rectangular tablets of the composition $(K_3FeC_6N_5O)_2 + 7H_2O$, which become anhydrous at 110°. 100 parts of water at 18° dissolve 148 parts of the salt. The solution is neutral to litmus and phenolphthaleïn, and gives the following reactions with solutions of metallic salts: cadmium chloride, a white precipitate soluble in hydrochloric acid; cobalt nitrate, a pale-pink precipitate, becoming blue when heated, but regaining its original colour on cooling, insoluble in hydrochloric acid; copper sulphate, an apple-green precipitate, insoluble in hydrochloric acid; ferrous ammonium sulphate, a white precipitate which immediately becomes blue on addition of nitric acid; manganese chloride, a bulky white precipitate, soluble in hydrochloric acid; ferric chloride, a violet coloration, and after one or two days a precipitate of the same colour, partially soluble in cold dilute hydrochloric acid; ammonium molybdate in nitric acid, a canary-yellow precipitate; auric chloride, a red-brown coloration; uranium nitrate, an orange-yellow precipitate, insoluble in acetic acid, but soluble in ammonium acetate solution.

When heated at 300—400°, out of contact with air, until evolution of gas ceases, the anhydrous salt loses 9·05 per cent., and yields 8·33 per cent. of carbonic oxide (calc. 8·47 per cent.), together with potassium cyanide and iron cyanides. The composition and properties of this compound involve the assumption of the existence of a trivalent radicle, *carbonyl-ferrocyanogen*, $<\overset{CO}{Fe}>Cy_5\equiv$.

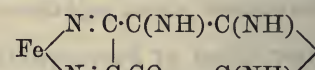
If a solution of the potassium salt is mixed with chlorine-water until it no longer gives a violet coloration with ferric chloride, a yellow solution is obtained which contains the carbonyl ferricyanide. It gives a violet-blue precipitate with ferrous sulphate, a white precipitate with mercurous nitrate, and with silver nitrate a maroon precipitate which rapidly becomes white. When this solution is

treated with sodium amalgam, it yields the ordinary ferrocyanide and the carbonyl ferrocyanide.

Friedel points out that the existence of this compound supports the formula for ferrocyanides which he proposed some years ago. According to this view, the ferrocyanides contain a ring of carbon-atoms. In Muller's compound, the group NH″ is replaced by the element O″ without any alteration of the nucleus.



Ferrocyanide.



Carbonyl ferrocyanide.

C. H. B.

Constitution of the Melamines. By B. Rathke (*Ber.*, **20**, 1056—1059).—The author considers that Ponomareff's observation that silver cyanurate reacts with alkyl iodides with formation of normal alkyl cyanurates, besides isocyanurates, decides the question of the constitution of cyanuric acid and melamine in favour of Hofmann's view (Abstr., 1886, 931). As the normal ethers readily change into isoethers, and the reverse reaction does not take place, the normal ethers must be the primary products of the decomposition.

The formula $NH<\begin{matrix}C(:NR)\cdot NH\\C(:NR)\cdot NH\end{matrix}>C:NR$ is suggested for triphenylmelamine as well as the nitrile formula $N\lessdot\begin{matrix}C(NHR):N\\C(NHR)\cdot N\end{matrix}\gtrdot C\cdot NHR$. The essential difference between these formulæ and that of the iso-compound $NR<\begin{matrix}C(NH)\cdot NR\\C(NH)\cdot NR\end{matrix}>C:NH$, is that whilst in the former the alkyl is contained in the side-chain, in the latter it is attached to the ring. N. H. M.

Thiammeline. By B. Rathke (*Ber.*, **20**, 1059—1065).—Thiammeline is readily obtained by direct combination of dicyandiamide with thiocyanic acid; the same compound has also been obtained by Klason by the action of potassium hydrosulphide on the substance $(CN)_3(NH_2)_2Cl$, obtained from cyanogen chloride and ammonia. Thiammeline functions both as an acid and a base; the *oxalate*, $(C_3H_5N_5S)_2C_2H_2O_4$, and *nitrate* crystallise in needles, the *sulphate* in leaflets; a *potassium* salt crystallising in needles, and a silver salt, a white precipitate, are described. A characteristic reaction of thiammeline is the production of a yellow, flocculent precipitate when a solution of its salt is boiled with copper sulphate and ammonia; when heated with concentrated hydrochloric acid, it is decomposed into cyanuric acid, ammonia, and hydrogen sulphide. Attempts to prepare an ethyl-derivative of thiammeline were unsuccessful, but with ethylene bromide an ethylenethiammeline hydrobromide, $C_5H_7N_5S,HBr$, was obtained, crystallising in colourless pyramids; the free base was not isolated. V. H. V.

Cocceryl Alcohol and Coccerylic Acid. By C. Liebermann and O. Bergami (*Ber.*, **20**, 959—966; comp. Abstr., 1885, 1045).—The

formula $C_{30}H_{62}O_2$, previously ascribed to cocceryl alcohol, is confirmed by further investigation. The *acetyl*-derivative, $C_{30}H_{60}(OAc)_2$, is obtained by heating two parts of the alcohol with one part of acetic anhydride at 170° for two hours; it forms snow-white crystalline flocks, melts at 48—50°, and is readily soluble in ether, warm alcohol, and acetic acid, very sparingly soluble in acetone. The *benzoyl*-derivative, $C_{30}H_{60}(OBz)_2$, is prepared by heating one part of cocceryl alcohol with two parts of benzoic anhydride at 210—220° for three hours; it forms white flocks, melts at 60—62°, does not readily solidify when heated above its melting point, and is less soluble than the acetyl-derivative in the solvents just mentioned. When oxidised with chromic acid in acetic acid solution, cocceryl alcohol is converted into a new pentadecylic acid, the chief product, a second acid of high melting point and sparing solubility, and a neutral compound.

Pentadecylic acid, $C_{15}H_{30}O_2$, is crystalline, melts at 59—60°, and is very readily soluble in alcohol, ether, benzene, and acetic acid, less soluble in light petroleum. It begins to boil at 257° under 100 mm. pressure, but the temperature rises during the distillation. The yield amounts to 40 per cent. of the cocceryl alcohol employed. Its *calcium* and *barium* salts were analysed; the *methyl* salt, $C_{15}H_{29}O_2Me$, is crystalline and melts at 66—68°.

Coccerylic acid is only partially oxidised with chromic acid in acetic acid solution, about 40 per cent. remaining unchanged. The chief oxidation product is pentadecylic acid (m. p. = 62°), and the yield amounts to 40 per cent. of the coccerylic acid employed.

W. P. W.

Oxidation of Polyatomic Alcohols. By E. Fischer and J. Tafel (*Ber.*, **20**, 1088—1094).—By the oxidation of polyatomic alcohols, carboxylic acids only have as yet been obtained; the aldehydes and ketones which are formed, have not been isolated as intermediate products, owing to the inefficiency of methods used.

In this paper, the phenylhydrazine test is employed to indicate the formation of those aldehydes and ketones, and a class of substance obtained which it is proposed to call the osazones.

Thus on warming glycerol with nitric acid (sp.gr. = 1·18), for a short time a violent reaction ensues; after removal of the nitrous acid with carbamide, a liquid is obtained, which reduces Fehling's solution, and gives with phenylhydrazine hydrochloride a crystalline substance of the composition $C_{15}H_{16}NO_4$, a *phenylglycerosazone*, which melts at 131° and decomposes at 170° with evolution of gas; it is sparingly soluble in hot water, readily in alcohol and ether. To it the constitutional formula $OH{\cdot}CH_2{\cdot}C(N_2HPh){\cdot}CH : N_2HPh$ is provisionally assigned, as more probable than the alternative formula

$$N_2HPh : CH{\cdot}CH(OH){\cdot}CH : N_2HPh.$$

In order to decide whether the product of oxidation is an aldehyde or ketone, the nature of the substance obtained by treatment of dibromacraldehyde with baryta is examined. After removal of the excess of baryta, the substance formed reduces Fehling's solution and gives with phenylhydrazine a crystalline precipitate of the composition $C_{18}H_{22}N_4O_4$, resembling phenylglucosazone in physical properties and

external appearance; it is probable that a glucose is formed in the reaction thus: $2C_3H_4Br_2O + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2$.

In like manner erythrol, on oxidation with dilute nitric acid, yields a substance which reduces Fehling's solution and gives with phenylhydrazine a crystalline substance, $C_{16}H_{18}N_4O_2$, melting at 166—167°, sparingly soluble in hot water, more readily in ether and benzene; the reaction with dulcitol is precisely similar. On the other hand, isodulcitol, although classified with the above hexatomic alcohols, differs from them in yielding a crystalline precipitate with phenylhydrazine without previous oxidation with nitric acid. This substance, $C_6H_{10}O_3(N_2HPh)_2$, crystallises in needles, melting at 180° with decomposition, soluble in alcohol and ether. Thus isodulcitol belongs rather to the aldehydic or ketonic alcohols, and its formula is probably $C_6H_{12}O_5$; it combines with water in like manner to chloral and glyoxylic acid; it is possibly the methyl-derivative of arabinose.

V. H. V.

A New Galactan. Properties of Galactose. By E. O. v. Lippmann (*Ber.*, **20**, 1001—1008).—The liquid obtained in the manufacture of sugar from the lime sludge after being freed from lime by means of carbonic anhydride and oxalic acid and evaporated down, yielded, when kept for two months, a thick, gelatinous precipitate. This was kneaded with water until the wash-water remained colourless, dissolved in boiling milk of lime, and the liquid evaporated whilst carbonic anhydride was passed in. It was then put into tall cylinders to settle, the clear liquid drawn off, evaporated, and when cold treated with excess of hydrochloric acid and precipitated with absolute alcohol. This operation was repeated and the gum purified by fractional precipitation with absolute alcohol; it was then kneaded under absolute alcohol and finally left in small pieces in alcohol. It then forms an almost white, brittle mass, very readily soluble in water (the impure substance is insoluble in cold water and alcohol). It has the formula $C_6H_{10}O_5$; the aqueous solution is dextrorotatory: $[\alpha]_D = +238°$ (in a 10 per cent. solution at 20°), it does not reduce Fehling's solution. When inverted with dilute sulphuric acid, it is completely converted into galactose; the name *γ-galactan* is therefore given to the compound.

The author's previous statement that galactose ferments when treated with yeast has been confirmed by Tollens, although according to Kiliani (*Ber.*, **13**, 2305) no fermentation takes place. N. H. M.

Preparation of Normal Propylamines and Isoamylamines. By H. Malbot (*Compt. rend.*, **104**, 998—1000).—Normal propyl alcohol and fermentation amyl alcohol were converted into the corresponding chlorides, and after purification these were heated with an equivalent quantity of ammonia in sealed tubes at 140—165° for 12 to 24 hours (see this vol., p. 356). The proportion of primary amine diminishes as the molecular weight of the radicle increases; it is one-fifth for the propylamines, one-tenth for the isobutylamines, and very small indeed for the isoamylamines. The formation of tertiary amines is probably due to a reaction between the primary amines first formed and the still unaltered alkyl chloride. C. H. B.

Homologues of Acetyl-acetone: Formation of Ketones of the Acetic Series. By A. Combes (*Compt. rend.*, **104**, 920—921).—Acetyl-acetone dissolves sodium with evolution of hydrogen and formation of a solid compound, $CHNa(COMe)_2$, which is soluble in ether and is decomposed by water into acetone and sodium acetate. If this sodium-derivative is heated with ethyl iodide in sealed tubes at 130—140°, it yields sodium iodide and *monethyl-acetyl-acetone*, $CHEt(COMe)_2$, a colourless liquid which boils at 175°, and is only slightly soluble in water. It dissolves with development of heat in a solution of sodium hydrogen sulphite, but no crystallisation takes place until the solution is cooled to a low temperature.

This reaction constitutes a general method for the preparation of the homologues of acetyl-acetone. With amyl iodide, the sodium-derivative yields amyl-acetyl-acetone which boils at 225°.

The second atom of hydrogen in the group CH_2 can also be displaced by sodium, and the disodium-derivatives react with alkyl iodides. It is thus possible to obtain diketones of the two types,

$$CH(C_nH_{2n+1})\cdot(COMe)_2 \text{ and } (COMe)_2 : C<\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}.$$

All the homologues of acetyl-acetone are decomposed into an acetate and a ketone when treated with an alkali. Ethyl-acetyl-acetone yields the methyl propyl ketone discovered by Friedel, and amyl-acetyl-acetone yields a liquid which boils at 170°, and is identical with the methyl hexyl ketone described by Béhal. The decomposition of diketones homologous with acetyl-acetone furnishes a new method for the preparation of ketones of the type $Me\cdot CO\cdot C_nH_{2n+1}$. All the stages in the operation give almost theoretical yields. C. H. B.

Fatty Acids occurring in Resin Oil. By J. Lwoff (*Ber.*, **20**, 1017—1023). The mixed sodium salts obtained by extracting resin oil with aqueous soda were treated with a concentrated solution of sodium chloride to precipitate such sodium salts as are insoluble in presence of salt; the supernatant liquid was poured off, treated with hydrochloric acid, and distilled. The acids were separated by conversion into amides. Valeric, œnanthylic, nonylic, and undecylic acids were isolated. The amides of the last two acids melt respectively at 77—78° and 80—81°, and both crystallise in lustrous plates soluble in hot water containing ammonia. N. H. M.

Octyl Mono-, Di-, and Tri-chloracetates. By G. Gehring (*Compt. rend.*, **104**, 1000—1001).—The octyl alcohol was obtained by the action of potassium hydroxide on castor-oil, and is therefore the secondary alcohol described by Bouis.

The ethereal salts were obtained by passing hydrogen chloride into a mixture of the alcohol and acid, or, in the case of the dichloracetate, of the alcohol and the potassium salt.

Octyl monochloracetate is a colourless, neutral, very mobile oil with an ethereal odour and a burning taste. It boils at 234°, produces a permanent stain on paper, burns with a green flame, and is insoluble

in water but dissolves in alcohol and ether in all proportions; sp. gr. at 10° = 0·9904.

The dichloracetate boils at 244°, and is a neutral, colourless, mobile liquid, lighter than water, and very similar in its properties to the monochloracetate, but its odour and taste are less marked. The trichloracetate boils at about 260°, and is a colourless oil with an ethereal odour. It is lighter than water, and closely resembles the two preceding compounds in its general properties. C. H. B.

Metallic Propionates. By A. Renard (*Compt. rend.*, **104**, 913—916).—*Aluminium propionate* cannot be isolated from its solution, which is decomposed on heating with almost complete precipitation of the basic compound $(C_3H_5O_2)_4OAl_2$. *Ammonium propionate*, syrupy, noncrystallisable, soluble in water and alcohol. *Barium propionate* crystallises simultaneously from the same solution in two forms: (*a*) bulky, transparent prisms, $(C_3H_5O_2)_2Ba + H_2O$, which become anhydrous at 110°; and (*b*) brilliant, transparent needles, $(C_3H_5O_2)_2Ba + 6H_2O$, which lose $3H_2O$ in dry air and become anhydrous at 110°, melt above 300°, and then decompose; insoluble in alcohol; 100 parts of water dissolve 54·1 of dry salt at 12° and 7·6 at 100°. *Calcium propionate*, $(C_3H_5O_2)_2Ca + H_2O$, brilliant flattened needles, which become anhydrous at 100° and melt above 300°; insoluble in alcohol; 100 parts of water dissolve 41·7 parts at 12° and 45·6 at 100°. *Cadmium propionate*, non-crystallisable syrup, soluble in all proportions in water and alcohol. *Chromic propionate*, obtained as the basic salt, $(C_3H_5O_2)_4OCr_2$, a hard, deep-violet, amorphous mass, by concentrating a solution of chromic hydroxide in propionic acid. *Cobalt propionate*, $(C_3H_5O_2)_2Co + 3H_2O$, forms wine-coloured crystalline crusts, which become anhydrous at 100°, melt at about 250° to an indigo liquid; very soluble in alcohol; 100 parts of water dissolve 35·5 parts at 11°; aqueous solution deep wine-red, becomes blue on heating. *Copper propionate*, $(C_3H_5O_2)_2Cu + H_2O$, emerald-green prisms which become anhydrous at 100° and decompose at 110°. The neutral solution, heated for some time at 100°, deposits the pale-blue basic salt, $(C_3H_5O_2)Cu,CuO + H_2O$. *Ferrous propionate*, greenish crystals which very rapidly oxidise. *Ferric propionate* forms a hard, friable, reddish-brown solid; its aqueous solution decomposes when heated, with precipitation of ferric hydroxide. *Lithium propionate*, $C_3H_5O_2Li + H_2O$, forms deliquescent crystals, which become anhydrous in dry air; 100 parts of water dissolve 66·4 parts of dry salt at 14° and 88·8 parts at 100°; 100 parts of alcohol of 95° dissolve 5·1 parts at 14° and 6·3 at its boiling point. *Magnesium propionate*, $(C_3H_5O_2)_2Mg + H_2O$, a white powder which becomes anhydrous at 100°, and is very soluble in water and alcohol. *Manganese propionate* forms a pale rose-coloured, syrupy mass which gradually crystallises; very soluble in water and alcohol. *Mercurous propionate*, $(C_3H_5O_2)_2Hg_2$, obtained by double decomposition, a white crystalline powder which melts at 225° and decomposes; 100 parts of cold water dissolve 1·4 parts of salt; boiling water decomposes the salt into mercury and mercuric propionate, but the decomposition is prevented by a few drops of propionic acid; the salt is also decomposed by

alcohol. *Mercuric propionate*, $(C_3H_5O_2)_2Hg$, forms needles which melt at 110° to a colourless liquid, and decompose at about 180° with loss of propionic acid and formation of mercurous propionate; 100 parts of water at 15° dissolve 19·2 parts; decomposed by water and by alcohol with separation of mercuric oxide. *Nickel propionate*, $(C_3H_5O_2)_2Ni + 2H_2O$, a pale-green syrup which slowly crystallises in dry air and becomes anhydrous at 100°. *Lead propionate*, $(C_3H_5O_2)_2Pb$, forms a thick syrup which very gradually changes to a soft, crystalline mass melting below 100°, and soluble in water and alcohol. If its solution is boiled with lead monoxide and filtered, the filtrate deposits small needles of the basic salt $(C_3H_5O_2)_2Pb,PbO$; 100 parts of water dissolve 8·8 parts of this basic salt at 20° and 6·3 parts at 85°. *Potassium propionate*, $C_3H_5O_2K + H_2O$, crystallises in soft deliquescent plates which become anhydrous at 120° and melt above 300°; 100 parts of water dissolve 178 parts of dry salt at 16° and 309 parts on boiling; 100 parts of alcohol of 95° dissolve 22·2 at 13° and 26·4 on boiling. *Potassium hydrogen propionate* forms deliquescent plates which do not lose propionic acid at 100°. *Sodium propionate*, $C_3H_5O_2Na + H_2O$, forms a soft, deliquescent, crystalline mass, which becomes anhydrous at 100°; 100 parts of water dissolve 99·1 parts of dry salt at 15° and 187 parts on boiling; 100 parts of alcohol of 95° dissolve 4·4 parts at 13° and 8·4 on boiling; no acid propionate is formed. *Strontium propionate*, $(C_3H_5O_2)Sr + 6H_2O$, crystallises in prismatic needles, which lose 3 mols. H_2O in dry air and melt in their water of crystallisation and become anhydrous at 100°; 100 parts of water dissolve 27 parts of dry salt at 12°; it is insoluble in alcohol. *Zinc propionate*, $(C_3H_5O_2)_2Zn + H_2O$, crystallises in needles which become anhydrous in dry air; 100 parts of water dissolve 32 parts of dry salt at 15°; 100 parts of alcohol dissolve 2·8 parts at 15° and 17·2 parts on boiling. C. H. B.

Chlorinated Derivatives of Crotonic Acid. By J. Wislicenus (*Ber.*, **20**, 1008—1110).—*α-β-Dichlorobutyric acid*, $C_4H_6Cl_2O_2$, is prepared by passing a strong current of chlorine through a solution of solid crotonic acid in carbon bisulphide. The solvent is evaporated, the residue freed by filtration from adhering oil, and crystallised several times from a small quantity of ether. It forms large, lustrous, colourless prisms which melt at 62·5—63°.

α-Chlorisocrotonic acid, $C_4H_5ClO_2$, is formed when *α-β*-dichlorobutyric acid is treated with an excess of aqueous soda. When the reaction takes place in a hot solution, *α*-chlorocrotonic acid is also formed; the two acids can be readily separated as potassium salts; the salt of the new acid being readily soluble in cold alcohol. It crystallises from water in needles melting at 66·2—66·5°. The *potassium* salt crystallises from alcohol in needles of a slightly silky lustre.

α-Chlorocrotonic acid melts at 99—99·5° (not 97·5°).

When liquid isocrotonic acid is treated with chlorine, a liquid product is formed which contains, however, solid *α-β*-dichlorobutyric acid. When treated with excess of alkali, *α*-chlorocrotonic acid (m. p. 99—99·5°) and *α*-chlorisocrotonic acid are formed.

α-Chlorisopropylene, C_3H_5Cl, is obtained by heating an aqueous solution of the potassium salt of solid *α-β*-dichlorobutyric acid. It resembles its isomeride and boils at 33·2—33·5°. Propylaldehyde is formed in the reaction. Ordinary *α*-chloropropylene can be obtained in like manner from liquid *α-β*-dichlorobutyric acid. (Compare A. Michael and G. M. Browne (next Abstract.)). N. H. M.

Isomerism in the Crotonic Acid Series. By A. Michael and G. M. Browne (*J. pr. Chem.* [2], **35**, 257—260).—The so-called *β*-bromocinnamic acid is not identical with the additive product of hydrobromic acid and phenylpropiolic acid (Abstr., 1886, 702). The *β*-bromocrotonic acid prepared from *α-β*-dibromobutyric acid is similarly not identical with the additive product prepared from tetrolic acid. Pure tetrolic acid when treated with hydrobromic acid at 0° deposits crystals which may be crystallised from light petroleum. It differs from its two isomerides in its melting point, 94·5—95°, and its solubility and crystalline form; the silver salt is amorphous and the barium salt crystallises with 1 mol. of water. H. B.

Synthesis in the Paraffin Series by Means of Aluminium Chloride. By A. Combes (*Compt. rend.*, **104**, 855—858).—If the compound $C_{12}H_{14}O_6,Al_2Cl_6$ (this vol., p. 127) is added in small portions to well-cooled alcohol, an energetic reaction takes place with evolution of hydrogen chloride, and when the product is poured into water a reddish liquid separates, which is a mixture of ethyl acetate, ethyl acetoacetate, and a colourless liquid which has the composition $C_8H_{12}O_4$, and boils at 120—125°; vapour-density 5·90. This is ethyl acetoacetylacetate, $CH_2Ac{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, and the formation of ethyl acetoacetate and ethyl acetate is due to the readiness with which it splits up in presence of alcohol and acetic acid. A solid product is also obtained, which is insoluble in water, but dissolves in warm alcohol, benzene, and light petroleum, and crystallises from these solvents in red prisms melting at 129—130°. It has the composition $Al_2(C_8H_{11}O_4)_6$, and is formed by the union of 6 mols. of ethyl acetoacetylacetate with 2 atoms of aluminium. It is very stable, and is not attacked by sulphuric or nitric acid in the cold, but its alcoholic solution is decomposed by alkalis with precipitation of the aluminium and formation of a crystalline compound.

When butyric chloride is treated in the same way as acetic chloride (*loc. cit.*), it yields a similar compound which boils at 216° under a pressure of 14 mm. and rapidly becomes solid. After recrystallisation it has the composition nC_4H_6O and melts at 107°. It does not volatilise without decomposition, but when its alcoholic solution is treated with alkalis it yields salts of the composition $C_{12}H_{19}O_4Na$, and therefore its formula is $C_{12}H_{18}O_3$. This compound is the anhydride of a diketonic acid, butyro-butyryl-butyric acid, the elimination of water from the molecule taking place in much the same way as in the formation of lactones. C. H. B.

Action of Bromine on Carbamide. By A. Smolka (*Monatsh. Chem.*, 8, 64—68).—The following experiments were undertaken in the

endeavour to obtain a bromine substitution product by the direct action of bromine on carbamide. When bromine is added drop by drop to a concentrated alcoholic solution of carbamide, the product consists almost entirely of ammonium bromide. Bromine and carbamide heated together in equivalent proportions yielded cyanuric acid, ammonium bromide, and free nitrogen; this forms a very convenient method for the preparation of the first named substance.

When bromine and carbamide are heated together in a sealed tube ammonium bromide and cyamelide are formed. G. H. M.

Antimony Tartrate. By Guntz (*Compt. rend.*, **104**, 850—852).—When an excess of antimony trioxide is boiled with an aqueous solution of tartaric acid, 1 mol. of the oxide is dissolved for every 5 mols. of acid present, no matter how long ebullition is continued, and this ratio is also independent of the concentration of the solution provided that it be not too dilute, in which case the solubility of antimony oxide in water affects the ratio. The free tartaric acid in the solution is determined by means of standard baryta with phenolphthaleïn as an indicator, and the antimony trioxide is determined by means of potassium permanganate. The solution is evaporated to a syrup, and on cooling deposits almost the whole of the antimony in the form of a crystalline acid tartrate, which is purified by washing with absolute alcohol. The original solution may also be evaporated to complete dryness and the excess of tartaric acid removed by treating the residue with alcohol, when the antimony tartrate is left in crystalline leaflets of the composition $C_4H_4O_5,SbO{\cdot}OH$.

Its heat of formation was determined by dissolving it in hydrofluoric acid, and also dissolving in the same acid a mixture of tartaric acid and antimony oxide in the same proportions.

Sb_2O_3 sol. + $2C_4H_6O_6$ sol. = $2C_4H_4O_5SbOOH$ sol. + H_2O sol. develops $-0{\cdot}5$ Cal. × 2.

Sb_2O_3 sol. + $2C_4H_4O_5KOH$ sol. = $2C_4H_4O_5SbOOK$ sol. + H_2O sol. develops $-0{\cdot}85$ Cal. × 2.

It is evident that the substitution of antimony oxide for hydrogen develops practically the same amount of heat whether the substitution takes place in tartaric acid or potassium hydrogen tartrate. Antimony hydrogen tartrate is decomposed by water but dissolves in a solution of tartaric acid. The heat of dissolution of antimony trioxide, Sb_2O_3, in tartaric acid (5 mols.) is $+11{\cdot}2$ Cal.

Berthelot obtained $+7{\cdot}1$ Cal. as the heat of formation of the antimony tartrate by dissolving antimony trichloride in tartaric acid. The author has likewise observed that the heat of formation seems to vary with the method of preparation, and further experiments are being made. C. H. B.

Constitution of Pyrotritartaric Acid. By C. Paal (*Ber.*, **20**, 1074—1077).—According to Fittig, the constitution of pyrotritartaric acid is best represented by the formula $<\begin{matrix}CO\cdot CH_2\\CH:CMe\end{matrix}>CH{\cdot}COOH$, that is, as an unsaturated ketonic acid and a derivative of pentamethylene.

But the recent investigations of the author, showing that the acid takes up at first four atoms of bromine to form a tetrabromo-acid, which is reconverted by hydrogenation into the original acid, and that this acid by the further addition of four atoms of bromine gives an additive product, as also yields a pentabromo-derivative, indicate that pyrotritartaric acid is analogous to and probably a derivative of pyromucic acid. This view is confirmed by its synthesis from ethyl acetonylacetoacetate and its reactions with phenylhydrazine and hydroxylamine; pyrotritartaric acid is then probably a dimethylfurfuranecarboxylic acid, $<\begin{matrix}O—CMe\\CMe:CH\end{matrix}>C\cdot COOH$.

V. H. V.

Derivatives of Pyrotritartaric Acid. By F. Dietrich and C. Paal (*Ber.*, **20**, 1077—1080).—Hitherto the derivatives of pyrotritartaric acid, with the exception of the salts, have not been investigated, owing to its indifference towards some reagents, and its complete decomposition by others. By bromination in chloroform solution, a tetrabromopyrotritartaric acid, $C_6H_3Br_4O\cdot COOH$, is formed, which crystallises in well-formed prisms melting at 161°, soluble in alcohol and ether, insoluble in water and petroleum; its metallic and ethereal salts are unstable. When treated with bromine, it takes up four more atoms of bromine to yield *tetrabromopyrotritartaric acid tetrabromide*, $C_6H_3Br_8O\cdot COOH$, which crystallises in short prisms melting at 168—170°; the salts of this acid are unstable, and it is completely decomposed by alkalis. On treating the tetrabromo-derivative with excess of bromine in sealed tubes, a pentabrominated acid, $C_6H_2Br_5O\cdot COOH$, is formed. This crystallises in elongated rhombohedra, and melts at 197°.

Wislicenus and Stadnicki found that when pyrotritartaric acid is treated with phosphoric chloride it yields an acid chloride, decomposed by water to re-form the acid; but if the reaction is conducted at a higher temperature, a dichloro-compound is formed; the latter is a colourless, heavy oil of disagreeable odour, converted by exposure to damp air into pyrotartaric acid and a resin.

During the distillation of carbopyrotritartaric acid, a dimethylfurfuran, identical with that obtained from acetonylacetone, together with pyrotritartaric acid and *uvinone*, are formed. This last substance, $C_{14}H_{12}O_4$, crystallises in tufts of needles, melting at 247·5°; with bromine, it yields an octabromo-derivative, $C_{14}H_4Br_8O_4$, crystallising in pyramidal prisms, sparingly soluble in most menstrua; when heated, it carbonises with evolution of bromine and hydrobromic acid.

V. H. V.

β-Bromofurfuran. By F. Canzoneri and V. Oliveri (*Gazzetta*, **17**, 42—44).—Two bromo-derivatives of furfuran are indicated by theory, namely, one in which the bromine displaces a hydrogen-atom in either of the CH groupings attached to the oxygen-atoms, and the second in which a hydrogen-atom is displaced in one of the CH groupings not attached to the oxygen. Both these substances have been obtained by the decomposition of the bromopyromucic acids. In order to prepare β-bromofurfuran, the corresponding bromopyromucic acid

is first purified from the dibromo-acid by means of its ethyl salt, which is saponified, and the acid obtained is then distilled with an equal weight of lime. *β-Bromofurfuran*, thus produced, is a colourless, transparent liquid, boiling at 103°, heavier than and insoluble in water. V. H. V.

Synthesis of Hemellithene. By O. Jacobsen and W. Deike (*Ber.*, **20**, 903—904).—Metaxylenesulphonic acid [Me : SO_3H : Me = 1 : 2 : 3] is obtained by sulphonating dibromometaxylene

[Me : Me : Br : Br = 1 : 3 : 4 : 6]

with chlorosulphonic acid, converting the sulphochloride formed into the sodium salt of the acid by means of alcoholic soda, and removing the bromine with zinc-dust and ammonia. When a hot solution of the sodium salt is treated with bromine dissolved in hydrochloric acid, the corresponding bromometaxylene is obtained, and this is converted into hemellithene by the action of sodium and methyl iodide in ethereal solution.

Bromometaxylene boils at about 206°, and does not solidify at −10°. W. P. W.

Reduction of Trinitro-ψ-cumene. By F. Mayer (*Ber.*, **20**, 966—973).—The constitution of the acid, $C_9H_{12}N_2SO_5$ (this vol., p. 36), obtained when trinitro-ψ-cumene is reduced with hydrogen sulphide, cannot be ascertained from an examination of its salts, which are unsatisfactory compounds, nor is it possible to characterise it either as a carboxylic acid or a mercaptan. If, however, it is heated with concentrated sulphuric acid at 140—150°, a considerable quantity of the sulphate of Fittig's nitro-ψ-cumidine (*Annalen*, **151**, 157), is obtained, and inasmuch as on heating either with concentrated hydrochloric acid or with water at 180°, it yields the same sulphate and also sulphuric acid, it follows that the compound must be regarded either as a nitro-ψ-cumidinesulphonic acid or as a nitro-ψ-cumidine-sulphaminic acid, $NO_2{\cdot}C_6HMe_3{\cdot}NH{\cdot}SO_3H$. The synthetical formation of the compound by heating nitro-ψ-cumidine sulphate with chlorosulphonic acid at 165° for four hours does not distinguish between the formulæ, and no evidence has been obtained to show which of the two is correct.

Acetylnitro-ψ-cumidinesulphonic acid, $C_9H_{11}N_2SO_5Ac$, melts at about 230° with decomposition, and is readily soluble in water and alcohol, sparingly soluble in ether.

The constitution of nitro-ψ-cumidine [Me : NO_2 : Me : Me : NH_2 = 1 : 2 : 3 : 4 : 6] and of nitro-ψ-cumidinesulphonic acid follows from the fact that both compounds, on reduction with tin and hydrochloric acid, yield meta-ψ-cumylenediamine [Me : NH_2 : Me : Me : NH_2 = 1 : 2 : 3 : 4 : 6], whilst the former, by elimination of the amido-group and subsequent reduction with stannous chloride, is converted into third ψ-cumidine which must have the formula [Me : NH_2 : Me : Me = 1 : 2 : 3 : 4].

Meta-ψ-cumylenediamine crystallises in long, hard needles, melts at 84°, and dissolves readily in benzene. Ferric chloride gives to its solution an intense dark-red colour. When treated with diazo-com-

pounds, chrysoïdines are obtained, whilst with nitrosodimethylaniline hydrochloride it yields a dye analogous to Witt's tolylene-red.

ψ-Cumidine boils at 236°, and does not solidify at −15°. Its *acetyl*-derivative, $C_9H_{12}NAc$, melts at 186°. This cumidine is probably identical with that obtained by Nölting and Forel (Abstr., 1886, 58). The corresponding nitrotrimethylbenzene melts at 30°.

W. P. W.

Action of Sulphuric Acid on Pentamethylbenzene. By O. Jacobsen (*Ber.* **20**, 896—902).—Pentamethylbenzene, obtained by the action of methyl chloride on mesitylene or pseudocumene in the presence of aluminium chloride, can readily be separated from the accompanying hexamethylbenzene by fractional crystallisation from alcohol; its purification from small quantities of durene and possibly of isodurene is, however, more difficult, and is best effected by sulphonating the impure hydrocarbon with chlorosulphonic acid. Pentamethylbenzene sulphone and sulphochloride are formed, and the latter is converted into the sodium sulphonate, separated from any durene-sulphonate by crystallisation, converted into the sulphonamide, and together with the sulphone saponified at 170° with concentrated hydrochloric acid. The *sodium*, *potassium*, *barium*, *calcium*, *silver*, and *copper* salts of pentamethylbenzenesulphonic acid are described; they are crystalline, anhydrous, and sparingly soluble in water; the *chloride*, $C_6Me_5{\cdot}SO_2Cl$, crystallises from ether in large, flat prisms, and melts at 82°; the *amide* forms large, flat prisms, showing a vitreous lustre, melts at 186°, is sparingly soluble in cold alcohol, and when oxidised with potassium permanganate yields a *sulphonamic* acid melting at about 265°. The *sulphone* crystallises in very long, slender, colourless needles, melts at 98·5°, is readily soluble in alcohol, and on distillation yields pentamethylbenzene.

When sodium pentamethylbenzenesulphonate is shaken with concentrated sulphuric acid and light petroleum, hydrolysis occurs and the pure hydrocarbon is obtained on evaporation of the latter. The sulphonic acid cannot be prepared by the action of concentrated sulphuric acid, inasmuch as pentamethylbenzene when repeatedly shaken with 3 to 4 times its weight of the acid during 36 to 48 hours, and then treated with ice, yields prehnitenesulphonic acid and a solid hydrocarbon, which is found to be hexamethylbenzene and not an octamethylanthracene (Abstr., 1886, 694). The action of sulphuric acid on durene (*loc. cit.*) may, therefore, be regarded as resulting in the formation of pseudocumene and pentamethylbenzene, the latter in the presence of the acid undergoing further change into prehnitine and hexamethylbenzene.

W. P. W.

Resorcinol-derivatives. By W. Will and W. Pukall (*Ber.*, **20**, 1119—1136).—Æsculetin has been recognised as a dihydroxy-derivative of coumarin, but the trihydroxybenzene, from which it is derived, has as yet not been isolated. The starting point of experiments made in this direction was the preparation of benzeneazo-resorcinol, $C_6H_3(OH)_2{\cdot}N_2Ph$ [OH : OH : N_2Ph = 1 : 3 : 4], from resorcinol, by means of the diazo-reaction. This substance, previously

described by other investigators, yields with ethyl iodide in presence of potash a mono- and a di-ethoxy-derivative. The former,

$$OH\cdot C_6H_3(OEt)\cdot N_2Ph,$$

crystallises in prisms resembling alizarin; it melts at 87°, is readily soluble in alcohol, insoluble in water; the latter crystallises in yellowish-red needles melting at 70·5°, soluble in alcohol and ether. On hydrogenation with tin and hydrochloric acid, the stannochlorides of aniline and amidodiethoxyresorcinol are produced. The hydrochloride of the latter exists in two modifications, namely, as glistening needles or a grey, crystalline powder, both of which melt at 198°, and are converted the one into the other according to the conditions of crystallisation. The free base, $C_6H_3(OEt)_2\cdot NH_2$, crystallises in broad needles melting at 32°; its salts are very soluble and readily oxidised; the *dibromo*-derivative crystallises in needles melting at 112°; the *acetyl*- and the *benzoyl*-derivatives melt at 120·5° and 113·5° respectively. When amidodiethoxyresorcinol is oxidised either by exposure to air or more readily by a ferric salt, a deep blue liquid is obtained, from which a violet-brown precipitate separates, and may be purified by sublimation. This compound, $C_{18}H_{21}NO_5$, is formed thus: $2C_6H_3(OEt)_2NH_2 + O_2 = C_{18}H_{21}NO_5 + NH_3 + EtOH$; it crystallises in steel-blue needles melting at 170°, and is soluble in alcohol, insoluble in ether. It is probably a derivative of quinone, of the formula $OEt\cdot C_6H_2O_2\cdot NH\cdot C_6H_3(OEt)_2$ [O : $NHC_6H_3(OEt)_2$: OEt : O = 1 : 2 : 3 : 4).

Amidodiethoxyresorcinol, on oxidation with chromic acid, yields an *ethoxyquinone*, $C_6H_3O_2\cdot OEt$ [O : OEt : O = 1 : 3 : 4], crystallising in yellow needles melting at 117°; it dissolves in water, and its solution gives on addition of a trace of amidoethoxyresorcinol a blue coloration from formation of the above intermediate condensation-product. *Ethoxyquinol*, $C_6H_3(OH)_2\cdot OEt$, obtained by reduction of the quinone with sulphurous acid, crystallises in colourless prisms melting at 112·5°, and is soluble in water, alcohol, and ether. The triethoxy-derivative, $C_6H_3(OEt)_3$, crystallises in glistening needles melting at 34°; from the corresponding phenol, æsculetin is derived.

Ethylamidoresorcinol, $OH\cdot C_6H_3(OEt)\cdot NH_2$ [OH : OEt : NH_2 = 1 : 3 : 4], prepared in a manner similar to the above diethoxy-compound, forms colourless needles melting at 148°, soluble in water and alcohol. On oxidation with chromic acid, it seems to yield a quinone.

V. H. V.

Resorcinol-derivatives. By W. Pukall (*Ber.*, **20**, 1136—1152). —*Diazodiethylresorcinol chloride*, $C_6H_3(OEt)_2\cdot N_2Cl$, obtained under particular conditions from amidodiethylresorcinol sulphate, is an unstable, crystalline substance, soluble in water with greenish-yellow coloration. By boiling water, as also by alkalis, it is readily converted into a diethylresorcinol, although the reaction is complicated by subsidiary changes, which lead probably to the formation of diresorcinol-derivatives. These substances were, therefore, separately examined.

Tetrethyldiresorcinol, $C_{12}H_6(OEt)_4$, prepared from diresorcinol and ethyl iodide in presence of alkali, crystallises in large, colourless

leaflets melting at 100°, soluble in ether, insoluble in water, acids, and alkalis.

Diethylresorcinolparazoresorcinol, $C_6H_3(OEt)_2{\cdot}N_2{\cdot}C_6H_3(OH)_2$, prepared from diazodiethoxyresorcinol and resorcinol, forms glistening green crystals melting at 193·5°, insoluble in water and dilute acids, readily soluble in alcohol.

Orthophenylazoethylresorcinol, $PhN_2{\cdot}C_6H_3(OH){\cdot}OEt$, obtained together with the para-derivative, in small quantities by the ethylation of crude phenylazoresorcinol, crystallises in carmine-red needles, melts at 150°, is readily soluble in alcohol and ether, and in contradistinction to the para-derivative, is soluble in alkalis. By further ethylation, it is converted into the diethyl-derivative, $PhN_2{\cdot}C_6H_3(OEt)_2$, which forms glistening tabular crystals melting at 90°, insoluble in water, acids, and alkalis. On reduction with tin and hydrochloric acid, it is converted into *orthamidodiethylresorcinol hydrochloride*,

$$C_6H_3(OEt)_2{\cdot}NH_2,HCl,$$

which crystallises in colourless needles; the free base crystallises in leaflets melting at 124°, soluble in alcohol, insoluble in water. On oxidation, it yields a compound, $C_{18}H_{20}N_2O_3$, the constitution of which was not further investigated; it crystallises in brown-red needles melting at 207°. Attention is drawn to the formation of an ortho-, together with a para,- derivative in the diazo-reaction. Liebermann considers that the production of the ortho-derivative in this reaction is more common than has been hitherto suspected, but the quantities formed are insufficient for their separation.

Diethylresorcinolorthazoresorcinol, $C_6H_3(OEt)_2N_2C_6H_3(OH)_2$, prepared from diazodiethoxyresorcinol and an aqueous solution of resorcinol, is a reddish-yellow, crystalline precipitate, melting at 182·5°, soluble in alcohol and ether, insoluble in water.

Experiments made with a view of obtaining the corresponding phenol led to no satisfactory results. V. H. V.

Triphenylthiammeline and a Third Triphenylammeline. By B. Rathke (*Ber.*, **20**, 1065—1074).—*Triphenylthiammeline*,

$$NH\!<\!\begin{matrix}C(NPh){\cdot}NPh\\ C(NPh)\!-\!\!-\!N\end{matrix}\!>\!C{\cdot}SH,$$

is obtained, together with other products, by heating triphenylthiodicyandiamine; it crystallises in leaflets melting at 238°, and is sparingly soluble in alcohol, moderately soluble in chloroform. It functions both as an acid and a base, forming with mineral acids crystalline salts, such as the hydrochloride and sulphate, and also dissolving in alkalis to form crystalline metallic derivatives, decomposed by carbonic anhydride. When heated with ethyl bromide and alcohol, triphenylthiammeline yields the hydrobromide of the corresponding mercaptide, $C_3N_5HPh_3{\cdot}SEt,HBr$. This crystallises in colourless, strongly refractive prisms, of neutral reaction, and is converted into triphenylammeline when boiled with alcohol. This substance, also obtainable from tetraphenylmelamine, crystallises in

colourless leaflets, often twinned, and melts at 275° (uncorr.); its *hydrochloride* crystallises in white needles, and the *platinochloride* is a yellow, crystalline precipitate. This substance seems to be isomeric with the two triphenylammelines described by Hofmann.

If the mercaptide above mentioned is heated with alcoholic ammonia, a *triphenylmelamine* is obtained, which crystallises in minute needles melting at 185—188°, and is moderately soluble in alcohol. This substance is isomeric with the three known triphenylmelamines; its probable constitution is discussed. V. H. V.

Primary and Secondary Xylylamines from Xylenols. By P. Müller (*Ber.*, **20**, 1039—1042).—When ammonio-zinc bromide (1 part), ammonium bromide (3 parts), and α-orthoxylenol [Me : Me : OH = 1 : 2 : 4] (1 part), are heated for 40 hours at 300°, xylidine boiling at 215—220° (the acetyl-derivative melts at 134°), and dixylylamine are obtained. The latter boils, with partial decomposition, at 330—345°; it solidifies to a glassy mass when cooled by means of a mixture of ether and carbonic anhydride.

α-Metaxylidine was prepared from α-metaxylenol in a manner similar to the ortho-compound. It is colourless, but soon becomes brown; it boils at 210—215°. The acetyl-derivative melts at 129·5°. The di-α-metaxylylamine, obtained in the same reaction, is an oil which boils at 305—310°. Like the diortho-derivative, it solidifies when treated with ether and calcium anhydride. N. H. M.

Aromatic Hydroxylamines. By A. Michael and G. M. Browne (*J. pr. Chem.* [2], **35**, 358—359).—When an alcoholic solution of picric chloride is treated with aqueous hydroxylamine, *dipicrylhydroxylamine*, $[C_6H_2(NO_2)_3]_2N{\cdot}OH$, is obtained. This forms yellow needles soluble in alcohol. If ethyl picrate is substituted for the chloride, *picrylhydroxylamine*, $C_6H_2(NO_2)_3{\cdot}NH{\cdot}OH$, is produced; this forms silky, yellow needles, is soluble in alcohol, ether, and glacial acetic acid, and melts at 99—100°. L. T. T.

Azo-compounds. By J. V. Janovsky (*Monatsh. Chem.*, **8**, 49—63; compare Abstr., 1886, 794 and 1024).—The bromazobenzene melting at 187°, and formerly described (*loc. cit.*) as monobromazobenzene, is the *dibromide*. *Parabromazobenzene* (N : Br = 1 : 4) melts at 82°, and crystallises in brilliant orange plates. It is easily soluble in hot and cold alcohol, ether, &c. When treated with nitric acid in glacial acetic acid solution, it yields two substances—(*a*) a *bromonitroazobenzene* (N : Br = 1 : 4) melting at 107—108° (uncorr.), and crystallising in yellow needles; when boiled with ammonium sulphide this gives amidobromazobenzene crystallising in brilliant plates; (*b*) a *paradinitroazobenzene*, melting at 190° and crystallising in woolly needles; when boiled with ammonium sulphide, this yields an amido-compound possessing strong tinctorial powers. When parabromazobenzene is treated with fuming sulphuric acid, a *bromazobenzenesulphonic acid*, $C_{12}H_8BrN_2{\cdot}SO_3H + 3H_2O$, is formed; it crystallises in orange-brown needles with a golden lustre; it gives well-defined, crystalline *sodium*, *potassium*, and *zinc* salts. The sodium salt is very insoluble in water.

The acid appears to be identical with the parazobenzeneparasulphonic acid previously described by the author (Abstr., 1884, 1146).

The metabromazobenzene previously described (*loc. cit.*), when treated with fuming sulphuric acid, yields *metabromazobenzenesulphonic acid*, $C_{12}H_8BrN_2{\cdot}SO_3H + 1\frac{1}{2}H_2O$, which gives very insoluble alkaline salts. The *potassium* salt is precipitated from a 1 per cent. solution of the chloride in the form of pearly needles; the *sodium* salt is also thrown down from a 1 per cent. solution of sodium chloride in yellow, nacreous needles.

When orthodibromazobenzene (*loc. cit.*) is treated with nitric acid in acetic acid solution, it yields a *trinitrodibromazobenzene*, melting at 135° and crystallising in red needles.

When orthonitroazobenzene, previously described (*loc. cit.*), is treated with bromine, it yields a *monobromonitroazobenzene*, melting at 132°.

Orthonitroazobenzene behaves towards reducing agents in a manner entirely different from paranitroazobenzene (*loc. cit.*). The substance with strong tinctorial powers previously described is now considered by the author to be *hexa-azoxybenzene*, $O\begin{<}{N—C_6H_4N : NC_6H_5 \atop N—C_6H_4N : NC_6H_5}$, an intermediate reduction product. It is an orange-yellow powder consisting of microscopic scales, and melts at 206° without decomposition. The mononitrosulphonic acids of azobenzene have been previously described by the author (Abstr., 1882, 834, and 1883, 867).

Orthoamidoazobenzene, the preparation of which has been previously described (*loc. cit.*), melts at 123°, and forms yellow needles with a brilliant lustre. Its salts are distinguished from those of ordinary amidoazobenzene by their form.

Another substance formed by the nitration of azobenzene in glacial acetic acid seems to be a *nitroazoxybenzene;* it melts at 122°, and forms red, pearly tables, often twinned like muscovite. When treated with bromine, it yields a bromine-compound, melting at 126°.

G. H. M.

Reaction of Diazoamido-compounds with Phenols. By K. Heumann and L. Œconomides (*Ber.*, **20**, 904—909).—Further investigation has shown that the formation of a hydroxyazo-compound by the action of diazoamidobenzene on phenol (this vol., p. 480) is also brought about when other diazoamido-compounds are employed. Diazoamidobenzene, when added to fused resorcinol and carefully heated, yields aniline and benzeneazoresorcinol (Abstr., 1878, 219). Diazoamidoparatoluene yields paratoluidine and paratolueneazophenol (this Journ., 1876, i, 268) when heated with phenol on a water-bath, and when added to fused resorcinol it forms paratoluidine and *paratolueneazoresorcinol*, $C_7H_7{\cdot}N_2{\cdot}C_6H_3(OH)_2$. This crystallises in yellowish-red needles, melts at 184°, and is readily soluble in alcohol, ether, benzene, and chloroform, yielding orange-coloured solutions. From diazoamidoparachlorobenzene and phenol, when heated on a water-bath, parachloraniline is obtained together with *chlorobenzeneazophenol*,

$C_6H_4Cl\cdot N_2\cdot C_6H_4\cdot OH$; this crystallises from chloroform in reddish-yellow needles, and melts at 151—152°. The action of phenol on diazoamidometabenzoic acid takes place more slowly than is the case with the foregoing diazoamido-compounds, but proceeds similarly, inasmuch as metamidobenzoic acid and phenolazobenzoic acid are obtained.

Hydroxyazo-compounds are also formed by the action of phenols on mixed diazoamido-compounds, and the results of the experiments are given in quantitative form. When diazoamidobenzeneparatoluene is heated with phenol at 100°, approximately equal weights of aniline and paratoluidine are obtained together with a compound melting at 122°, and consisting of two hydroxyazo-compounds which have not yet been separated. Diazoamidobenzeneparatoluene and resorcinol heated on a water-bath yield aniline, paratoluidine, and a hydroxyazo-compound. On heating diazoamidoparachlorobenzenebenzene and phenol at 90°, parachloraniline and hydroxyazobenzene were obtained, whilst diazoamidoparachlorobenzeneparatoluene and phenol heated first at 80—90° and afterwards at 110°, yield parachloraniline and paratolueneazophenol. W. P. W.

Cinnamyl Hydrazine. By L. Knorr (*Ber.*, **20**, 1107—1108).—In order to examine whether the formation of pyrazoline-derivatives from phenylhydrazine and acids of the acrylic series is analogous to the formation of pyrazole-derivatives from unsaturated ketones, cinnamyl hydrazine was prepared and its products of decomposition investigated. The hydrazide, $C_{13}H_{14}N_2O$, prepared from cinnamic acid or its ethereal salt, crystallises in minute needles which melt at 183°. On dry distillation, an oil passes over which solidifies in the crystalline form; its composition is expressed by the formula $C_{15}H_{12}N_2O$; it melts at 251°, is insoluble in water, sparingly soluble in alcohol and ether, readily in alkalis and acids. It is proposed to carry on further investigations on homologous compounds. V. H. V.

Phenazoxine—a New Chromogen. By A. Bernthsen (*Ber.*, **20**, 942—944).—*Phenazoxine*, $C_6H_4<^{NH}_{-O-}>C_6H_4$, is obtained when equimolecular proportions of catechol and orthamidophenol are heated at 260—280° for 40 hours, and after treating the residue with water and aqueous soda, can be extracted from it by ether. It crystallises in bright, colourless scales, melts at 148°, distils with slight decomposition, and is readily soluble in alcohol, ether, benzene, and chloroform, sparingly soluble in light petroleum. When treated with concentrated nitric acid, it yields a crystalline *nitro*-derivative, which on reduction with tin and hydrochloric acid, and subsequent oxidation with ferric chloride, is converted into a reddish-violet dye; the reaction corresponding with the formation of Lauth's violet (thionine) from thiodiphenylamine. Phenazoxine dissolves in concentrated sulphuric acid with a violet-red colour, and its alcoholic solution yields a dark bluish-green coloration with ferric chloride, and a deep blue with bromine-water. W. P. W.

Action of Dehydrating Agents on Benzylideneacetoxime. By N. Zelinsky (*Ber.*, **20**, 922—924).—*Benzylideneacetoxime*,

$$CHPh : CH\cdot CMe : NOH,$$

is obtained when benzylideneacetone (1 mol.) dissolved in alcohol is added to a solution of hydroxylamine hydrochloride ($1\frac{1}{2}$ mol.) and sodium hydroxide ($1\frac{1}{2}$ mol.) in aqueous alcohol, and the whole heated for some hours on the water-bath. It is crystalline, melts at 115—116°, boils without decomposition at 220° under 100 mm. pressure, and with bromine yields an additive compound, melting at 144—145° with decomposition.

With acetic chloride, an acetyl-derivative, $CHPh : CH\cdot CMe : NOAc$, is obtained, melting at 90—91°. Sulphuric acid does not effect a condensation, but phosphoric anhydride, or still better, phosphorus oxychloride reacts with benzylideneacetoxime yielding an oil having basic properties. W. P. W.

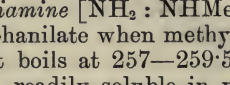
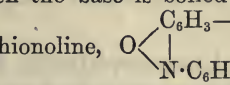
Methyl- and Ethyl-orange, and the Derived Dimethyl- and Diethyl-thionines. By A. Bernthsen and A. Goske (*Ber.*, **20**, 924—934).—*Methyl-orange* (sodium methylamidoazobenzenesulphonate), $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NHMe$, is obtained by diazotising sulphanilic acid and gradually adding the product to an aqueous solution of pure methylaniline hydrochloride heated at 30°; reddish-violet needles separate in large quantity, and when filtered off are dissolved in aqueous soda. It crystallises in large, orange-red laminæ, and is readily soluble in hot, but only sparingly soluble in cold water. The yield amounts to 30 per cent. of the theoretical quantity.

Sodium diazomethylamidobenzenesulphonate, $SO_3Na\cdot C_6H_4\cdot N_2\cdot NMePh$, is formed together with methyl-orange in the process just mentioned if dilute solutions are employed, and the product is kept nearly neutral throughout by the continued addition either of aqueous soda or of sodium acetate; the methyl-orange is decomposed by heating with concentrated ammonium sulphide at 100° the product obtained on addition of salt to the solution, the diazoamido-compound remaining unaffected. It crystallises in white or very pale-yellow scales, is readily soluble in hot water, insoluble in alcohol, and is not affected by boiling with dilute alkali. Although colourless, it shows all the properties of a diazoamido-compound: thus, dilute acids convert it into the corresponding amidoazo-acid; when heated with concentrated hydrochloric acid, it yields methylaniline and paraphenolsulphonic acid, and when warmed with an acetic acid solution of resorcinol it yields the yellowish-brown coloration characteristic of diazoamido-compounds. The authors find, moreover, that paradiazoamidotoluene, when heated with ammonium sulphide at 100°, is obtained on cooling in large, transparent, thin prisms of a pale-yellow colour, although diazoamidobenzene does not lose its yellow colour when similarly treated.

Ethyl-orange (sodium ethylamidoazobenzenesulphonate) is prepared by a method similar to that used to obtain the methyl-compound, with the exception that the mixed solutions are kept nearly neutral throughout with aqueous soda. It crystallises in orange-red laminæ.

The *acid* crystallises in glistening, bluish-violet needles, melts at about 244° with decomposition, and is insoluble in cold water and hot alcohol.

Methylparaphenylenediamine [$NH_2 : NHMe = 1 : 4$] is obtained together with sodium sulphanilate when methyl-orange is warmed with ammonium sulphide. It boils at 257—259·5°, does not solidify in a freezing mixture, and is readily soluble in water, alcohol, and ether. The *sulphate*, $(C_7H_{10}N_2)_2,H_2SO_4$, crystallises in needles. The corresponding ethylparaphenylenediamine (this vol., p. 244) can be obtained similarly from ethyl-orange; its *sulphate*, $C_8H_{12}N_2,H_2SO_4$, crystallises in long, colourless needles or thin prisms.

Dimethylthionine,  , is obtained by the action of ferric chloride and hydrogen sulphide on methylparaphenylenediamine in acid solution; at the same time, a red compound analogous to methylene-red is also formed. The base is sparingly soluble in ether and alcohol, and the alcoholic solution shows a red fluorescence. The *hydrochloride* dissolves in water with a beautiful blue colour, and shows a reddish-brown fluorescence; the *hydriodide* is a dark-blue powder, soluble in hot water and hot alcohol; it dyes silk an almost pure blue. When the base is boiled with much water, it is converted into methylthionoline,  , and when further saponified with 70 per cent. sulphuric acid yields thionol (Abstr., 1886, 53).

Diethylthionine obtained in a similar manner from ethylparaphenylenediamine, very closely resembles dimethylthionine in the colour of solutions, and the positions of the absorption-bands of the two compounds are almost identical. The maximum absorption of the darker band lies between C and D and near $\lambda' = 625$, that of the lighter band near $\lambda'' = 580$ to 585. W. P. W.

Action of Nitrous Acid on Orthoamidobenzamide. By A. Weddige and H. Finger (*J. pr. Chem.* [2], **35**, 262—264).—Equimolecular proportions of sodium nitrite and a salt of orthoamidobenzamide are mixed in aqueous solution, when a yellowish-brown crystalline substance separates. Its composition is represented by the formula $C_7H_5N_3O$, it melts at 213°, and is easily soluble in alkalis. The following derivatives are described: the sodium salt, $C_7H_4NaN_3O$; the ammonium and silver salts; and the methyl salt, $C_7H_4MeN_3O$, which can also be obtained by the action of nitrous acid on orthoamidobenzomethylamide; the constitution of the substance $C_7H_5N_3O$ is thus determined to be $C_6H_4<^{CO\cdot NH}_{-N:N-}>$. H. B.

Oximes of Paraxyloquinone. By J. Sulkowski (*Ber.*, **20**, 977—981).—*Paraxyloquinoneoxime*, $C_6H_2Me_2O : NOH$ [$Me : O : Me : NOH = 1 : 2 : 4 : 5$], is obtained, together with a small quantity of the dioxime, when 10 grams of paraxyloquinone dissolved in 300 cc. of

80 per cent. alcohol is boiled with 5 grams of hydroxylamine hydrochloride for two hours. It crystallises in small, yellowish needles, melts at 168°, and is insoluble in water, readily soluble in alcohol, ether, and benzene. On reduction with tin and hydrochloric acid, it yields *paramidoxylenol hydrochloride*, crystallising in small needles; the base forms silvery scales, and melts at 242° with decomposition.

Paraxyloquinonedioxime is formed, together with an equal proportion of the monoxime, when twice the above quantity of hydroxylamine hydrochloride is employed. It is crystalline, melts at about 272°, and is insoluble in water, very sparingly soluble in hot alcohol, benzene, and acetic acid. The *diacetyl*-derivative crystallises in small, yellow prisms, melts at 170°, and is readily soluble in hot alcohol and benzene, insoluble in dilute alkalis. When reduced with tin and hydrochloric acid, the dioxime yields *diamidoxylene hydrochloride;* this crystallises in white, glistening scales, and the base forms scales melting at 142° with decomposition.

When paramidoxylenol is heated with chloranil in acetic acid solution, a beautiful bluish-violet dye is obtained, together with tetrachloroquinol. The dye is insoluble in water, but soluble in alcohol, ether, benzene, and acetone, alkalis dissolve it with a pure blue colour, and the bluish-green solution in sulphuric acid shows a general darkening of the red end of the spectrum; analyses point to the formula $C_{24}H_{26}N_2O_3$. W. P. W.

Bromorthotoluic and Bromophthalic Acids. By C. Nourrisson (*Ber.*, **20**, 1016—1017).—*Bromorthotolunitrile*, $C_6H_3MeBr\cdot CN$ [1 : 5 : 2], is prepared from bromorthotoluidine by Sandmeyer's reaction; it crystallises from alcohol in long needles which melt at 70°; it distils readily with steam. When 10 grams of the nitrile are boiled with a solution of 10 grams of caustic soda in 100 c.c. of alcohol for 1½ hours, a mixture of bromotoluic acid and its amide is obtained. The latter dissolves in 10 parts of boiling alcohol, and separates in lustrous plates melting at 180°: it sublimes in needles which melt at 181—182°. When treated with concentrated alcoholic potash solution, or with diluted sulphuric acid, it is converted into bromorthotoluic acid,

$$[Me : COOH : Br = 1 : 2 : 5],$$

melting at 187°. When bromorthotoluic acid is oxidised with potassium permanganate, it is converted into β-bromophthalic acid, $[COOH_2 : Br = 1 : 2 : 5]$; this is very soluble in warm water, and melts at 168°; the anhydride melts at 106—108°, and boils at 297—301°. 70 grams of bromorthotoluidine yielded 60 grams of nitrile, and then 56 grams of toluic acid and 53 grams of crude bromophthalic acid. N. H. M.

Reduction of the Isomeric Bromocinnamic Acids. By A. Michael (*J. pr. Chem.* [2], **35**, 357—358).—The author has succeeded in reducing the so-called α- and β-bromocinnamic acids to cinnamic acids by treating their solutions in glacial acetic acid with zinc-dust No evolution of hydrogen takes place until 2 or 3 drops of platinum chloride has been added to the mixture. The acids appear to show

slight differences of crystalline form, &c., but whether this is due to traces of impurities merely is now being investigated. L. T. T.

Mono- and Di-hydroxytoluic Acids. By S. Weinreich (*Ber.*, **20**, 981—983).—Hydroxytoluic acid can readily be obtained from paratoluidine by converting it into the nitrile by Sandmeyer's reaction, saponifying this with sulphuric acid, sulphonating the toluic acid with concentrated sulphuric acid at 150—160°, and fusing the potassium salt of the resulting sulphotoluic acid with four times its weight of potassium hydroxide.

Dihydroxytoluic acid is prepared by heating paratoluic acid with crystallised sulphuric acid and phosphorus pentoxide at 250°. The barium salt, $COOH{\cdot}C_6H_2Me(SO_3)_2Ba + 5H_2O$, of the disulphotoluic acid obtained was analysed. On fusing the potassium salt with potassium hydroxide, dihydroxytoluic acid is obtained; this sublimes in colourless needles, melts at 175—176°, and is readily soluble in water, alcohol, and ether, sparingly soluble in benzene, toluene, and light petroleum. W. P. W.

Ethyl Phthalate Chloride and its Decomposition with Ethyl Sodiomalonate. By N. Zelinsky (*Ber.*, **20**, 1010—1013).—*Ethyl phthalate chloride*, $COOEt{\cdot}C_6H_4{\cdot}COCl$, is obtained by the action of phosphorus trichloride on sodium ethyl phthalate in presence of benzene or toluene as diluent; the solutions should be kept as cool as possible. The compound could not be isolated. When the solution in benzene, after being poured off from the phosphorous acid formed in the reaction, is treated with ethyl sodiomalonate suspended in benzene, a reaction takes place with separation of sodium chloride. The product is filtered, distilled in a vacuum until free from hydrocarbon and unchanged ethyl malonate, and the residue gradually treated with alcoholic potash. A potassium salt is obtained which is washed with alcohol, dissolved in water, and treated with sulphuric acid; the acid thus liberated is recrystallised from ether. It has the formula $C_{21}H_{16}O_{10}$, and melts rather above 180° with evolution of carbonic anhydride. When the product of the reaction is treated with an excess of alcoholic potash, a potassium salt different from that first obtained is formed; it yields an *acid* of the formula

$$C(COOH)_2(CO{\cdot}C_6H_4{\cdot}COOH)_2,$$

of which the acid $C_{21}H_{16}O_{10}$ is the *monethyl salt*, $C_{19}H_{11}EtO_{10}$.

N. H. M.

Action of Phenylhydrazine on Anhydrides of Bibasic Acids, and especially on Phthalic Anhydride. By B. Hötte (*J. pr. Chem.* [2], **35**, 265—298).—When phenylhydrazine and phthalic anhydride in molecular proportion are intimately mixed, phenylhydrazinephthalic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NHPh$, already described by Pellizzari (Abstr., 1886, 1025), is formed. The author finds the melting point to be 165—166°. The name *anilidophthalaminic acid* is proposed as most appropriate for this substance. When heated at 160—170°, this compound loses water, and is converted into phthalylphenylhydrazine (Abstr., 1886, 353). The author was quite unable

to obtain the isomeric compound melting at 210°, said by Pellizzari (*loc. cit.*) to be formed at the same time. The constitution of the above compound is $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot NHPh$.

α-Phthalyldiphenylhydrazine, $C_6H_4 : (CO)_2 : N\cdot NPh_2$, is prepared by heating phthalic anhydride and diphenylhydrazine at 150—170°; it crystallises in greenish-yellow plates, is soluble in alcohol, and melts at 154—155°.

α-Phthalylbenzoylphenylhydrazine, $C_6H_4 : (CO)_2 : N\cdot NBzPh$, is obtained when α-phthalylhydrazine and benzoic chloride in molecular proportion are heated together at 160—170°. It forms small, monoclinic tables, soluble in benzene, alcohol, and ether, and melts at 193°. When heated in closed tubes with fuming hydrochloric acid, it yields phenylhydrazine, and phthalic and benzoic acids. *α-Phthalylnitrosophenylhydrazine*, $C_6H_4 : (CO)_2 : N\cdot NPh\cdot NO$, is formed by treating the hydrazide suspended in ether with nitrous anhydride. It crystallises in pale yellow, rhombic tables, sparingly soluble in ether, and melting at 153—154°. During one preparation of this substance, the author obtained a substance crystallising in white scales, and decomposing with explosive violence slightly above 80°. The substance soon became brown, and decomposed to a thick liquid of irritating odour. The nitroso-compound can also be obtained by passing nitrous anhydride into glacial acetic acid in which the hydrazide is suspended, if care be taken to keep the mixture cool. If the current of anhydride is continued until the mixture becomes green, *α-phthalylnitrophenylhydrazine*, $C_6H_4 : (CO)_2 : N\cdot NPh\cdot NO_2$, is obtained. This forms yellow, rhombic tables, soluble in alcohol and ether, and melts with decomposition at 147—148°. With aqueous potash, it is decomposed into phthalic acid, phenylhydrazine, and potassium nitrite. If nitrous anhydride be passed into a hot acetic solution of α-phthalylphenylhydrazine, *α-phthalyldinitrophenylhydrazine* is formed. This is soluble in glacial acetic acid, from which it is precipitated in yellow flocks on the addition of water. It melts with decomposition at 182°, and is also decomposed by boiling alcohol or water. The one nitro-group has undoubtedly displaced the imidic hydrogen, but the position of the second is doubtful. When α-phthalylphenylhydrazine is heated with alcoholic ammonia in closed tubes at 70—80° for about three hours, *phthalylphenylhydrazidamide*, $NH_2\cdot CO\cdot C_6H_4\cdot CO\cdot N_2H_2Ph$, is formed. It is soluble in alcohol, nearly insoluble in ether, and crystallises in white plates melting at 146°. When heated at 160—170°, or when boiled with dilute alcohol, ammonia is evolved and β-phthalylphenylhydrazine (see below) is formed; the latter is also produced when the heating of the closed tubes is extended much beyond three hours.

When phthalic anhydride is mixed with excess of phenylhydrazine, reaction occurs as above, but if the mixture is heated at 150° for three or four hours, *phthalyldiphenyldihydrazine* (*dianilidophthalyldiamide*), $C_6H_4(CO\cdot NH\cdot NHPh)_2$, is formed; this crystallises in white tables melting at 191°. When heated with dilute hydrochloric acid, it is decomposed into α-phthalylphenylhydrazine and phenylhydrazine. If, however, the diamide is heated alone at 160—170°, phenylhydrazine is eliminated and *β-phthalylphenylhydr-*

azine, $C_6H_4<\begin{matrix}CO\cdot NH-\\CO\cdot NPh\end{matrix}>$, is formed. This is also produced if the original mixture is heated at 160—170°. It crystallises in colourless prisms soluble in boiling alcohol, chloroform, and ether, and in alkalis, and melts at 210°. This compound has already been obtained by Pellizzari (*loc. cit.*), but its formation is undoubtedly due to the intermediate formation of the diamide, and not to the direct action of phthalic anhydride and phenylhydrazine in molecular proportion, as stated by Pellizzari. Its ammonium salt yields with silver nitrate a white voluminous precipitate, $C_6H_4<\begin{matrix}CO\cdot NAg\\CO\cdot NPh\end{matrix}>$, soluble in ammonia, and unaltered by light. The *ethyl salt* crystallises in white needles soluble in alcohol and ether, and melts at 105—106°. When β-phthalylphenylhydrazine is heated with excess of benzoic chloride at 200°, *β-phthalylbenzoylphenylhydrazine*, $C_6H_4<\begin{matrix}CO\cdot NBz\\CO\cdot NPh\end{matrix}>$, is formed. It is crystalline, and melts at 122°, and has a faint odour of ethyl benzoate.

When benzoylphenylhydrazine and phthalic anhydride are heated together at 180°, *phthalylphenylbenzohydrazinic acid*,

$$COOH\cdot C_6H_4\cdot CO : NPh\cdot NBz,$$

is formed. It crystallises in white prisms melting at 172°, and soluble in alcohol. If the acid is heated alone, or the original mixture is heated at 220° for about a day, benzoic acid is eliminated, and β-phthalylphenylhydrazine formed.

When phenylhydrazine is heated with succinic anhydride, *α-succinylphenylhydrazine*, $C_2H_4 : (CO)_2 : N\cdot NHPh$, is obtained whether the hydrazine is in excess or not. It crystallises in white plates melting at 155°, and with nitrous acid yields a *nitroso-derivative* forming yellow, feathery crystals melting at 83—84°. No corresponding β-compound could be obtained.

Maleic anhydride yields with phenylhydrazine *maleïylphenylhydrazine*, $C_2H_2 : (CO)_2 : N\cdot NHPh$. It crystallises in needles which darken at 180°, and melt at 258—259°. If excess of the hydrazine is used, a dark brown, resinous mass is formed, from which no crystalline substance could be isolated. L. T. T.

Ethyl Triphenylcarbinylmalonate and β-Triphenylpropionic Acid. By G. G. Henderson (*Ber.*, **20**, 1014—1015).—*Ethyl triphenylcarbinylmalonate*, $CPh_3\cdot CH(COOEt)_2$, is prepared by adding ethyl sodiomalonate to an ethereal solution of triphenylcarbinyl bromide. It crystallises from boiling absolute alcohol in slender needles melting at 133·5°.

β-Triphenylpropionic acid, $CPh_3\cdot CH_2\cdot COOH$, is obtained by saponifying the above ethyl salt with alcoholic potash. It melts at 177°, is almost insoluble in water, soluble in alcohol, and very readily soluble in ether. The *sodium salt* (with 1 mol. H_2O) is readily soluble; the *barium salt* (with 1 mol. H_2O) crystallises in needles sparingly soluble in hot water; the *silver salt* is insoluble in water. N. H. M.

Action of Ethyl Sodacetoacetate and Ethyl Sodiomalonate on the Ethyl Salts of Unsaturated Acids. By A. MICHAEL (*J. pr. Chem.* [2], **35**, 349—357).—When ethyl sodiomalonate is added to an alcoholic solution of ethyl cinnamate, it dissolves, and if the solution is allowed to remain for some time, or is heated for a short time at 100°, and then mixed with water, an oil is obtained. This oil boils with partial decomposition at 305—310°, but under 15 mm. pressure distils without change at 213—215°. It has the constitution

$$COOEt{\cdot}CH_2{\cdot}CHPh{\cdot}CH(COOEt)_2.$$

When saponified with strong potash or baryta, the ether yields *phenylglutaric acid*, $COOH{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}COOH$, which crystallises in prisms easily soluble in alcohol and ethyl acetate, sparingly in benzene, insoluble in water; it melts at 137·5—138·5°. The *silver salt* is stable towards light.

When ethyl sodacetoacetate is substituted for ethyl sodiomalonate in the above reaction, a similar additive product seems to be formed, but the author has not yet isolated it, as it decomposes on boiling, even in a vacuum. The aqueous layer, however, contains a compound, $C_{15}H_{16}O_4$, which is probably formed by the elimination of sodium methylate from the additive compound first formed. It crystallises in needles soluble in alcohol, and melts at 139·5—140·5°. It shows the properties of a monobasic acid, and yields a *silver salt* crystallising in needles.

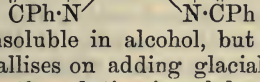
Ethyl citraconate and ethyl sodacetoacetate yield an additive compound, $C_{15}H_{24}O_7$, which forms a colourless oil, boiling at 173—174° under 26 mm. pressure. The aqueous layer also contains an acid, which, however, has not yet been isolated. These results show that in the action of ethyl sodiomalonate on ethyl α-bromacrylate lately described by the author (this vol., p. 468), the action need not necessarily be due to the direct elimination of sodium and bromine, but that an additive product may first be formed, and sodium bromide be afterwards eliminated. This reaction is therefore not a proof that Perkin's trimethylene-derivatives are open-chain derivatives.

The author finds that ethyl disodomalonate does not act on ethyl succinate in the cold, but that at high temperatures it seems to split up into ethyl sodiomalonate and sodium ethylate, and then ethyl succinosuccinate is formed. L. T. T.

Formation of Indigo-blue from Orthonitrophenolpropiolic Acid by Means of Potassium Cyanide. By A. MICHAEL (*J. pr. Chem.* [2], **35**, 254—256).—A solution of sodium orthonitrophenylpropiolate, when heated with pure potassium cyanide and a little glucose, gives rise to the formation of indigo-blue, even in the presence of a large excess of hydrocyanic acid. With potassium cyanide alone, nothing but intermediate products seem to be formed. The action is to be regarded as one of simultaneous oxidation and reduction.

H. B.

Derivatives of Benzidine. By P. BRUNNER and O. N. WITT (*Ber.*, **20**, 1023—1030).—*Tetramidodiphenyl*, $C_{12}H_6(NH_2)_4$, is obtained by warming orthodinitrobenzidine with stannous chloride and hydro-

chloric acid. The product is warmed with tin, diluted, and treated with hydrogen sulphide. It is then filtered and quickly evaporated in a current of hydrogen sulphide; the *hydrochloride* separates in white needles (with 2 mols. H_2O). This is very readily soluble in water, and is precipitated on adding hydrochloric acid. The free base crystallises in plates of a silvery lustre, resembling benzidine; it becomes black when filtered, and therefore could not be analysed. The *sulphate*, $C_{12}H_6(NH_2)_4 \cdot H_2SO_4$, crystallises in slender, white needles, very sparingly soluble in water, alcohol, and ether. When the acetate is treated with phenanthraquinone hydrogen sulphite (2 mols.) a *condensation product* is obtained. It is sparingly soluble, and sublimes in yellow needles. Sulphuric acid dissolves it with a fine violet colour, which, when the solution is diluted, changes to red, orange, and yellow. When the acetate is treated with a solution of benzil in glacial acetic acid, the *compound*  is formed. It is a whitish-yellow substance, insoluble in alcohol, but readily soluble in phenol, from which it crystallises on adding glacial acetic acid. It does not melt at 270°. When the solution in sulphuric acid is carefully diluted, the *sulphate* crystallises in lemon-yellow needles.

The properties of tetramidodiphenyl and its power of condensing with orthodiketones, show that the four amido-groups form two pairs in the ortho-position; this, together with the fact that amido-groups in the original benzidine used have the para-position, points to the constitution $C_6H_3(NH_2)_2 \cdot C_6H_3(NH_2)_2$ [$NH_2 : NH_2 : C_6H_3(NH_2)_2 = 4 : 3 : 1$] for tetramidodiphenyl. In Strackosch's dinitrobenzidine (*Ber.*, **5**, 236), the nitro-groups have the meta-position. When it is diazotised and the product boiled with alcohol, *dinitrodiphenyl*, $C_6H_4(NO_2) \cdot C_6H_4(NO_2)$ [$NO_2 = 3$], is obtained almost quantitatively. The latter crystallises from alcohol and glacial acetic acid in small yellow needles. It is dichroic, and melts at 197—198°.

Symmetrical metadiamidophenyl, $C_6H_4(NH_2) \cdot C_6H_4(NH_2)$ is prepared by reducing the nitro-compound with tin and hydrochloric acid. It is obtained as an oil, which solidifies after some days, and is sparingly soluble in water, readily in ether. The *diacetate* forms long needles, insoluble in water, sparingly soluble in alcohol, toluene, and cumene, more readily in phenol and glacial acetic acid. It melts at 257—258°. The *sulphate* crystallises in long needles, insoluble in cold water, sparingly soluble in alcohol. When the base is diazotised, and the product treated with sodium naphthionate, an isomeride of Congo-red is obtained; this forms a reddish-yellow solution in water. Unmordanted cotton-wool is dyed by it an orange colour; the colour is not so deep, and is less readily obtained than in the case of Congo-red.

N. H. M.

Derivatives of Diphenylethane. By K. Heumann and J. Wiernik (*Ber.*, **20**, 909—915).—The authors find that diamidodibenzyl (*Annalen*, **137**, 260), tetramethyldiamidodiphenylethane (Abstr., 1879, 714), and the dihydroxydiphenylethane obtained when the former is diazotised, are not leuco-compounds, since they do not

give dyes but only pale-brown, green, or colourless products when treated with various oxidising agents.

The *methiodide* of tetramethyldiamidodiphenylethane,

$$NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe_2,MeI,$$

is formed when diamidodibenzyl is heated with methyl iodide and a small quantity of potassium hydroxide at 150—180° for some hours; it cannot, however, be converted into the base by heating it with hydrochloric acid at 150°, whilst when heated to incipient fusion it yields a new base crystallising in small crusts. In the preparation of tetramethyldiamidodiphenylethane by Schoop's method (*loc. cit.*), an oily base is also formed, and can be separated from it by cooling.

W. P. W.

Tetramethyldiamidobenzophenone. By J. H. Ziegler (*Ber.*, **20**, 1111—1113).—Contrary to the observations of Münchmeyer, tetramethyldiamidobenzophenone readily yields a condensation-product with phenylhydrazine hydrochloride; the hydrazide obtained crystallises in groups of needles, melting at 174—175°, soluble in ether, light petroleum, and benzene. With concentrated sulphuric acid, it forms a red salt, dissolving in sulphuric acid with red coloration; on addition of water the red changes to yellow, with evolution of hydrochloric acid. The hydroxide gives Liebermann's reaction, and with oxidising agents yields a light-green, and subsequently a brown coloration.

V. H. V.

Synthesis of Juglone. By A. Bernthsen and A. Semper (*Ber.*, **20**, 934—941).—α-Hydroxyphthalic acid [OH : COOH : COOH = 1 : 2 : 3] is obtained when finely powdered juglone is gradually added to an alkaline solution of hydrogen peroxide, and the product, after treatment with sulphuric acid, is extracted with ether. This result confirms the author's view that juglone has the constitution [OH : O : O = 1′ : 1 : 4] (Abstr., 1885, 548; 1886, 363), which is further supported by the synthetical formation of the compound from 1 : 4′ dihydroxynaphthalene on oxidation. When dihydroxynaphthalene (Proc., 1887, 43), made into a thin paste with water, is treated with an excess of chromic mixture and allowed to remain for 24 hours, a *hydroxynaphthaquinone* separates, and after purification is found to be identical with juglone. The acetyl-derivative and the oxime of the synthetical compound are likewise identical with the corresponding juglone-derivatives.

The *diacetyl*-derivative of 1 : 4′ dihydroxynaphthalene is crystalline, melts at 159—160°, and is converted into acetyljuglone on oxidation with chromic mixture.

W. P. W.

1 : 3 Naphthylenediamine. By C. Urban (*Ber.*, **20**, 973—974).—The dinitronaphthalene (m. p. = 144°) obtained on diazotising Liebermann and Hammerschlag's dinitronaphthylamine (this Journal, 1876, ii, 80), yields 1 : 3 naphthylenediamine when reduced with tin and hydrochloric acid, inasmuch as the product reacts as a metadiamine with nitrous acid, and with diazo-compounds yields a chry-

soïdine. The *hydrochloride*, $C_{10}H_6(NH_2)_2,2HCl$, is readily soluble in water, soluble in alcohol, and sparingly soluble in ether; the *acetyl*-derivative crystallises in colourless, transparent prisms, melts at 154—156°, and is readily soluble in benzene. W. P. W.

β-Naphthyl-derivatives. By E. Bamberger and O. Boekmann (*Ber.*, **20**, 1115—1119).—*β-Naphtholthiamide*, $C_{10}H_7{\cdot}CS{\cdot}NH_2$, obtained by digesting β-naphthonitrile with ammonium sulphide, crystallises in long, pale-yellow needles, melting at 149°, and soluble in alcohol and ether, as also in hot water, but with decomposition into the nitrile and hydrogen sulphide. The thiamide, on hydrogenation with zinc and hydrochloric acid, yields *β-naphthylmethylamine hydrochloride*, $C_{10}H_7{\cdot}CH_2{\cdot}NH_2,HCl$, which crystallises in flat prisms, melting at 260—270°; the *platinochloride* and picrate forms sparingly soluble needles. The free base crystallises in glistening thick prisms; it absorbs carbonic anhydride from the air with great avidity, and is sparingly soluble in cold, more readily in hot water and alcohol. By nitrous acid, the amine is converted into the corresponding *naphthyl carbinol*, $C_{10}H_7{\cdot}CH_2{\cdot}OH$, crystallising in silky needles, melting at 80—80·5°; when oxidised with chromic mixture, it yields the *aldehyde*, $C_{10}H_7{\cdot}CHO$, which crystallises in a similar form, and melts at 60·5—61°. This aldehyde has previously been obtained from β-naphthoic acid, as also from naphthyl chloride; it reduces ammoniacal solutions of silver, gives a red coloration with rosaniline sulphite, and a leuco-base with zinc chloride and dimethylaniline.

V. H. V.

Nitrosanthrone. By A. Gimbel (*Ber.*, **20**, 974—977).—When nitrosoanthrone (Abstr., 1881, 99) is treated with various reducing agents, a small yield of a base is obtained, which readily oxidises in the air, with the loss of its basic properties and of a portion of its nitrogen. On heating equimolecular proportions of nitrosoanthrone and bromine dissolved in carbon bisulphide at 75°, dibromanthracene (m. p. 221°) is formed together with nitrous acid and nitric oxide, but no hydrogen bromide; whilst when bromine alone acts on the compound, a mixture of bromine additive-compounds of brominated anthracene is obtained. These are white, amorphous powders, melt at about 260° with evolution of bromine, and are converted into high brominated anthracenes by the action of alcoholic potash. When nitrosoanthrone is heated with concentrated hydrobromic acid at 260°, the above dibromanthracene is formed; concentrated hydrochloric acid at 180° converts it into a mixture of mono- and dichloranthracene, and with carbonyl chloride in benzene solution at 160° it yields dichloranthracene. W. P. W.

Action of Hydrogen on Nitro-derivatives of Terebenthene. By C. Tanret (*Compt. rend.*, **104**, 917—919).—When the hydrazocamphenes, the nitro-derivatives of essence of terebenthene, $C_{10}H_{17}{\cdot}NO_2$, are subjected to the action of nascent hydrogen (from iron and dilute sulphuric acid), until they give no violet coloration with ferric chloride, they yield bases with peculiar properties.

These bases have the same composition, $C_{20}H_{34}N_2O_2$, and the same reactions, but like their generators differ in their physical properties. They are anhydrous, dissolve very readily in alcohol, ether, and chloroform, volatilise somewhat below their melting point, and emit a camphoraceous odour when sublimed.

The α-compound forms flattened, lanceolate crystals which melt at 190°, and boil at about 300°, with gradual decomposition; soluble in 12 parts of water at 13°, but more soluble in boiling water; rotatory power $[\alpha]_D = +50°$.

Two compounds, β and β', are obtained from β-hydrazocamphene, which is thus resolved into two constituents. They can be separated by taking advantage of their different solubilities in water. The β-compound crystallises in rhomboidal tables which melt at 67°, and boil at about 290°; soluble in 10 parts of water at 13°, less soluble in hot water; rotatory power $[\alpha]_D = +27°$. The β'-compound forms slender needles which melt at 128°; soluble in 40 parts of water at 13°, and in 30 parts at 100°; rotatory power $[\alpha]_D = +8°$.

These compounds are neutral to litmus. When heated for a long time in sealed tubes with potash or hydrochloric acid, they yield no ammonia, and therefore are not amines. With acids they form well-defined, crystallisable salts, which, however, are somewhat unstable. Their solutions give precipitates with tannin, iodine solution, and potassium mercuric iodide. From these reactions, it is evident that they are closely related to the neutral alkaloïds, such as caffeïne and narcotine.

α-Dihydrocamphene sulphate, α-$C_{20}H_{34}N_2O_2,H_2SO_4$, exists only in acid solutions, and is completely decomposed by water. The hydrochloride, α-$C_{20}H_{34}N_2O_2,2HCl$, obtained by evaporating a solution of the base in the concentrated acid, is somewhat more stable in presence of water, but effloresces in the air and loses hydrogen chloride. The nitrate, α-$C_{20}H_{34}N_2O_2,2HNO_3$, crystallises from water without decomposition, and is more stable than the chloride, in presence of air. All these salts are very soluble in chloroform, but in presence of a suitable quantity of water they give up their acid to the water, like the salts of caffeïne.

The platinochloride, $(C_{20}H_{34}N_2O_2)_2,6HCl,PtCl_4$, is obtained by mixing concentrated solutions of the chloride and platinic chloride. The mercuro-chloride, $C_{20}H_{34}N_2O_2,HgCl_2$, is prepared by adding mercuric chloride to a solution of dihydrocamphene. If a large excess of soda is poured into the solution of the mercuro-chloride, a crystalline powder of the composition $C_{20}H_{34}N_2O_2,HgO$ is precipitated. This base dissolves in 70 parts of water at 13°, and in 30 parts at 100°, crystallises in slender, white needles, is not volatile, becomes coloured at 225°, and melts to a brown liquid at 260°; rotatory power $[\alpha]_D = +47°$; soluble in ether and chloroform. It has an alkaline reaction, and with some acids it forms salts, but others, such as sulphuric acid, decompose it immediately. When neutralised with hydrochloric acid, it yields a salt of the same composition as dihydrocamphene mercurochloride. It follows that dihydrocamphene mercurochloride is really the hydrochloride of a mercurial base, *hydrargyrine*.

C. H. B.

Terpinol. By G. Bouchardat and R. Voiry (*Compt. rend.*, **104**, 996—998).—The terpinol described by previous observers has been a mixture of substances obtained by several different reactions.

Terpin was boiled with very dilute sulphuric acid, the product distilled with water, and then fractionated, when it separated into two parts, one boiling at 170—176°, under ordinary pressure, and the other at 130—135°, under a pressure of 40 mm. When the second fraction is distilled, it yields a viscous liquid, with an odour of hyacinths, which remains liquid indefinitely, but if brought in contact with a crystal of caoutchene monohydrate, is slowly converted into a crystalline mass of the composition $C_{10}H_{18}O$, identical or isomorphous with caoutchene monohydrate. The crystals melt at 30—32°, and readily remain in superfusion, the sp. gr. of the liquid being 0·952. It boils at 218°, without alteration under ordinary pressure, and is inactive like terpene and caoutchene monohydrates. When treated with hydrogen chloride, it is completely converted into a dihydrochloride, $C_{10}H_{18}Cl_2$, and water.

The formation of this compound shows that terpinol contains an inactive monohydrate of terpilene, for which the authors propose the name terpilenol or terpol.

The first fraction has the composition $(C_{10}H_{16})_2,H_2O$, and remains liquid even at −50°; sp. gr. at 0° = 0·900, and is intermediate between that of the preceding hydrate and that of the hydrocarbon; vapour-density, 4·66. When fractionated with a Le Bel tube, with six bulbs, the fractions all have the same sp. gr. 0·905—0·902. The authors consider that this fraction may be regarded as containing a compound of the terpilenic hydrocarbon, $C_{10}H_{16}$, with the hydrate already described, this compound decomposing on volatilisation into the hydrocarbon and the monohydrate, a supposition which will explain the abnormal vapour-density. The production of such a compound mixed with an excess of either the hydrocarbon or the monohydrate, would explain the contradictory results of previous observers.

With hydrogen chloride, this fraction behaves like the monohydrate, and yields a readily crystallisable dihydrochloride.

C. H. B.

Manufacture of Santonin. By A. Busch (*J. pr. Chem.* [2], **35**, 322—341).—The author has been investigating some of the difficulties met with in the process of the extraction (on the manufacturing scale) of santonin from wormwood (*Artemisia maritima*). He gives an historical account of the growth of this industry.

The large percentage of resin obtained during the separation of santonin from its lime compound is due mainly to too high a temperature being employed, and to too little lime being originally added. At high temperatures, hydrochloric acid causes much of the base to resinify. The quantity of lime added to the original extract should be about 20 per cent., as otherwise much organic impurity is obtained in the solution. Part of the loss of santonin is also due to its absorption by the animal charcoal with which it is treated during the process of purification.

The santonin resin is not a homogeneous substance, but a mixture

of products of decomposition. Metallic salts, and especially lead salts (lead acetate), do not precipitate santonin from its alcoholic solutions, but do precipitate the santonin resins, and may be therefore used as a means of separating these. L. T. T.

Conversion of Pyrroline into Pyridine-derivatives. By G. Ciamician (*Gazzetta*, **17**, 11—17).—Ciamician and Dennstedt have shown that potassium pyrroline is converted by chloroform or bromoform into monochloro-, or bromo-pyridine (Abstr., 1882, 867). It would appear probable, *à priori*, that by the method of synthesis parachloropyridine would be produced, whereas the experiments of Lieben, and Staitinger, and those of Weidel show that the meta-derivative is produced. In order to explain this, it is suggested that the formation of chloro- or bromo-pyridines may be represented thus: $C_4H_4NH + CHCl_3 = C_4H_3ClNCH + 2HCl$; consequently the halogen, no longer united to that carbon-atom which makes up the pyridine nucleus, replaces a hydrogen-atom in the meta-position. Such an explanation affords no account, however, of the similar formation of chloropyridine by means of carbon tetrachloride. In order to throw further light on this question, the reaction of benzal chloride, $C_6H_5{\cdot}CHCl_2$, with potassium pyrroline is studied with a view of obtaining the metaphenylpyridine, isolated by Skraup. It is shown by analysis, as also by the physical properties of the platinochloride, and of the picrate, that this phenylpyridine is identical with Skraup's compound. In view of these experiments, it is remarked that the formula for pyrroline proposed by R. Schiff can no longer be preferred to that of Baeyer, the latter of which illustrates more completely the relationship of pyridine, indole, thiophen, and furfuran. V. H. V.

Pyrazole-derivatives. By L. Knorr (*Ber.*, **20**, 1096—1106).—In order to examine the nature of the isomerism of the diphenylmethylpyrazoles obtained by treating phenylhydrazine with ethylic benzoylacetoacetate and benzalacetoacetate respectively, various methylphenyl-derivatives of pyrazole and pyrazoline were examined.

Phenylhydrazinobenzalacetone, $C_{16}H_{16}N_2$, obtained from phenylhydrazine and benzalacetone, crystallises in yellow needles melting at 156°, and is insoluble in water, soluble in hot alcohol and acetic acid. When distilled, it is converted into a mixture of 1 : 5 : 3 diphenylmethylpyrazole and 1 : 5 : 3 diphenylmethylpyrazoline; the latter is separated by its solubility in ether; it crystallises in large prisms.

Phenyldimethylpyrazolecarboxylic acid, $<\begin{matrix}NPh{\cdot}CMe\\N{=}CMe\end{matrix}>C{\cdot}COOH$, is obtained as an ethyl salt from phenylhydrazine and ethyl ethylideneacetoacetate or ethyl acetylacetoacetate; it crystallises in needles melting at 197°; it is almost insoluble in water and dilute acids, sparingly soluble in ether and petroleum; its silver, copper, and lead salts are amorphous precipitates; the ethyl salt forms colourless crystals melting at 68°, and boiling at 286° under a pressure of 260 mm. The acid, when heated above its melting point, gives off carbonic anhydride, and is converted into phenyldimethylpyrazole,

[Ph : Me_2 = 1 : 3 : 5], an oil boiling at 273°, of feeble basic character, insoluble in water and alkalis, soluble in alcohol, ether, and acids. When heated with methyl iodide, it yields a *methiodide*, $C_{11}H_{12}N_2,MeI$, melting at 190°, soluble in alcohol and chloroform.

On treating phenyldimethylpyrazole with sodium amalgam, it is converted into the corresponding pyrazoline, $C_{11}H_{14}N_2$, a liquid boiling at 290°; this may also be obtained from phenylhydrazine and ethylideneacetone. V. H. V.

Syntheses of Quinoline-derivatives by means of Ethyl Acetoacetate. *γ*-**Hydroxyquinaldine.** By M. Conrad and L. Limpach (*Ber.*, **20**, 944—959).—When aniline and ethyl acetoacetate in molecular proportion are allowed to remain in the cold, or heated at 100° for some hours, ethyl anilacetoacetate is obtained. This compound, which the authors consider to be ethyl *β*-phenylamido-*α*-crotonate, NHPh·CMe : CH·COOEt, decomposes when rapidly heated at 240° for a few minutes, and yields a distillate amounting to 40 per cent., consisting chiefly of ethyl alcohol, acetone and carbanilide, and a viscid residue from which water extracts *γ-hydroxyquinaldine;* the yield of this compound amounts to 26 per cent. At the same time, ethyl phenyllutidonemonocarboxylate is also obtained, and the relative proportions of the two compounds depend on the temperature and duration of the heating.

γ-Hydroxyquinaldine, [OH : Me = 2′ : 4′], crystallises from water with 2 mols. H_2O in glistening prismatic crystals; these become anhydrous at 114°, and have a solubility of 1 in 10 parts of boiling, and 1 in 100 parts of cold water, the solution being feebly alkaline. The anhydrous compound melts at 230—231°, distils above 360° with much decomposition, and is readily soluble in alcohol, very sparingly soluble in ether, benzene, and light petroleum. It has an intensely bitter taste, is not volatile with steam, and its aqueous solution yields an intense reddish-yellow coloration with ferric chloride. The *mercurochloride* forms slender needles; the *chromate* is sparingly soluble, and melts at 106—108°; the *picrate* crystallises in slender, bright-yellow needles, and melts at 200°; the *hydrochloride*, $C_{10}H_9NO,HCl$, is crystalline, and the *platinochloride*,

$$(C_{10}H_9NO)_2,H_2PtCl_6,$$

forms bright yellow, matted needles, melts at 215°, and is sparingly soluble in cold water. On oxidation with potassium permanganate acetylanthranilic acid is obtained.

γ-Hydroxyquinaldine, when treated with bromine-water in the cold, yields a yellow additive-compound, which after a time is converted into a white *dibromo-derivative*, $C_{10}H_7Br_2NO$; an excess of bromine-water converts it into a white *tribromohydroxyquinaldine*, $C_{10}H_6Br_3NO$, melting at 275°.

Nitro-γ-hydroxyquinaldine, $C_{10}H_8(NO_2)NO$, is obtained when hydroxyquinaldine is heated with nitric acid (sp. gr. 1·4); it crystallises in slender needles, melts above 270°, and is very sparingly soluble in benzene or alcohol. On reduction with tin and hydro-

chloric acid, it yields *amido-γ-hydroxyquinaldine;* this forms white, prismatic crystals, decomposes at 225° without melting, and is very sparingly soluble in ether, readily soluble in alcohol and hot water, the aqueous solution showing a bluish fluorescence. The *hydrochloride*, $C_{10}H_8NO{\cdot}NH_2,HCl + H_2O$, forms white crystalline tufts.

γ-Chloroquinaldine, $C_{10}H_8NCl$, is obtained in almost the theoretical quantity by heating anhydrous γ-hydroxyquinaldine with phosphorus pentachloride at 130—140°. It melts at 42—43°, boils when carefully dried, at 270° without decomposition, and is sparingly soluble in water, readily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. The *picrate* crystallises in tufts of long needles, and melts at 178°; the *platinochloride*, $(C_{10}H_8NCl)_2,H_2PtCl_6$, is a yellow, crystalline precipitate. Chloroquinaldine when heated with water at 220° is converted into γ-hydroxyquinaldine, and when dissolved in acetic acid saturated with hydrogen iodide, and heated at 250—270° for eight hours, is reduced to quinaldine. On treatment with bromine-water in the cold, chloroquinaldine appears to form an orange-coloured additive-compound with 4 atoms of bromine, but when this is heated with alcohol, ethyl bromide is evolved, and the *hydrobromide* of chloroquinaldine, $C_{10}H_8NCl,HBr$, is obtained in white, acicular crystals.

Phenylamidoquinaldine, [Me : NHPh = 2′ : 4′], is obtained by heating equimolecular proportions of chloroquinaldine and aniline at 190°. It crystallises in prisms, melts at 150—151°, and dissolves sparingly in ether, but readily in alcohol and hot benzene.

Methoxyquinaldine, [Me : OMe = 2′ : 4′], is formed when chloroquinaldine (1 mol.) and methyl alcohol are heated with sodium methoxide (1 mol.) at 130—140° for two hours. It crystallises in long, slender needles, melts at 82°, distils at 294—298° without decomposition, and is sparingly soluble in hot water, readily soluble in alcohol and ether. It has a peppermint-like taste, an alkaline reaction, and is only slightly volatile with steam. The *mercurochloride* melts at 232°.

Methyl-γ-quinaldone, [Me : Me : O = 1′ : 2′ : 4′], can be obtained either by heating methoxyquinaldine in a sealed tube at 315°, or by heating γ-hydroxyquinaldine with methyl iodide at 120° for two to three hours. It forms white acicular crystals, fuses at 156°, melts at 160°, and is readily soluble in water, alcohol, and boiling benzene, sparingly soluble in ether. It has a pure bitter taste. The *mercurochloride* crystallises in slender, matted needles, and melts at 187°; the *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6$, is crystalline and melts at 240° with decomposition.

When γ-chloroquinaldine in a moist or impure state is heated to the distilling point, a vigorous reaction occurs and the whole is suddenly converted into a bluish-violet mass; this is insoluble in ether, but dissolves in alcohol and water, with an intense bluish-violet coloration. The compound is the hydrochloride of a colour-base, $C_{30}H_{22}N_3Cl,2HCl$; the base itself is insoluble in water, readily soluble in alcohol and ether, melts at about 220°, and yields intensely blue salts with acids. W. P. W.

Methylnaphthaquinolines and β-Naphthacridine. By J. H. Reed (*J. pr. Chem.* [2], **35**, 298—322).—C. Beyer has shown (Abstr., 1886, 629) that dimethylquinoline is formed when aniline acts on a mixture of acetone and paraldehyde, and cincholepidine when the paraldehyde is replaced by methylal. The author carried out similar syntheses in the naphthalene series.

Dimethyl-β-naphthaquinoline, $C_{10}H_6<\begin{matrix}CMe:CH\\-N:CMe-\end{matrix}>$, is formed when a cooled mixture of one part of paraldehyde and two of acetone is saturated with hydrogen chloride, β-naphthylamine hydrochloride (obtained by mixing β-naphthylamine with strong hydrochloric acid) then added, and the whole heated on the water-bath. The base crystallises in broad needles, soluble in alcohol, acetone, ether, glacial acetic acid, carbon bisulphide, and chloroform. It is only very sparingly soluble in boiling water and very slightly volatile in steam. It melts at 126—127°, and distils with partial decomposition above 300°. The *picrate* crystallises in small yellow needles, sparingly soluble in alcohol, ether, and acetone, and melting at 215°. The *dichromate*, $(C_{15}H_{13}N)_2,H_2Cr_2O_7$, crystallises in orange needles, sparingly soluble in pure water, easily so in water slightly acidified with sulphuric acid; it melts with decomposition at 115°. The *platinochloride*, $(C_{15}H_{13}N)_2,H_2PtCl_6 + 2\frac{1}{2}H_2O$, yields small needles. The *hydrogen sulphate*, $C_{15}H_{13}N,H_2SO_4$, crystallises in small needles; the *nitrate* in thick needles melting at 181°; the *methiodide*, $C_{15}H_{13}N,MeI$, in brownish needles. When nitrous anhydride acts on the base, either in the presence or absence of water, the nitrate is alone formed, no nitro- or nitroso-derivative being produced. When bromine acts on excess of the base in ethereal solution, the compound $(C_{15}H_{13}NBr_2)_2,HBr$ is formed as an orange, crystalline powder, melting at 207°. When boiled with 90 per cent. alcohol and animal charcoal, this substance is converted into the *bromide* of the base, $C_{15}H_{13}N,HBr + 2H_2O$, crystallising in white needles. *Dimethyl-β-naphthaquinolinesulphonic acid*, $C_{15}H_{12}N\cdot SO_3H + 1\frac{1}{2}H_2O$, is obtained by dissolving the base in 5 parts of cold fuming sulphuric acid, and pouring the product into water. It crystallises in small, colourless needles which melt without decomposition, and yield crystalline *potassium* and *copper* salts. If the solution in fuming acid be heated for an hour at 150—160°, it yields the *disulphonic acid*, $C_{15}H_{11}N(SO_3H)_2 + 4\frac{1}{2}H_2O$, which crystallises in needles, very soluble in alcohol, ether, and water: when heated, it decomposes without previous fusion. The *copper salt* crystallises with $5H_2O$, the *barium salt* with $7H_2O$. When fused with potash, the disulphonic acid yields *dimethyl-β-hydroxynaphthaquinolinesulphonic acid*, $OH\cdot C_{15}H_{11}N\cdot SO_3H + 1\frac{1}{2}H_2O$. This crystallises in yellow needles, and when heated decomposes without previous fusion. The dihydroxy-base could not be obtained. When oxidised with potassium permanganate, the base yields *β-dimethylphenylpyridinedicarboxylic acid*, $C_{13}H_{11}N(COOH)_2$. The free acid is a syrup, and gives a white *silver salt*.

Dimethyl-α-naphthaquinoline is formed when α- is substituted for β-naphthylamine in the above reaction. It crystallises in thick colourless needles, which are easily soluble in light petroleum,

sparingly so in alcohol, and melt at 43—44°. The *picrate* crystallises from alcohol in long, yellow needles melting at 223°. The *platinochloride* forms an unstable, yellow, crystalline precipitate. Bromine and methyl iodide form crystalline derivatives.

When a mixture of methylal and acetone is saturated with hydrogen chloride, β-naphthylamine hydrochloride added, and the whole heated on the water-bath, *methyl-β-naphthaquinoline* is formed together with small quantities of *β-naphthacridine*, and a base, $C_{24}H_{20}N_2$. β-Naphthacridine crystallises in straw-coloured needles melting at 216°. Its *picrate*, *hydrochloride*, *sulphate*, and *nitrate* are sparingly soluble in alcohol. This β-naphthacridine is also produced when no acetone is employed, and is probably due to the formation, during the reaction, of formaldehyde from the methylal. The base $C_{24}H_{20}N_2$ crystallises in short prisms, melting at 202—203°. The author considers that it is most likely *methyl-β-amidonaphthylhydroquinoline*. The *picrate* and the *methiodide* are both crystalline. Methyl-β-naphthaquinoline crystallises in needles, melts at 112°, and forms a crystalline picrate.

The author believes that the naphthacridine is formed according to the equations :—

$$2C_{10}H_7\cdot NH_2 = NH(C_{10}H_7)_2 + NH_3 ;$$

$$NH(C_{10}H_7)_2 + H\cdot COH = C_{10}H_6\begin{<}\begin{matrix}CH\\|\\N\end{matrix}\end{>}C_{10}H_6 + H_2O + H_2.$$

L. T. T.

Skatole from Strychnine. By C. Stoehr (*Ber.*, **20**, 1108—1111).—In a former paper (this vol., p. 604), the author showed that the product of distillation of strychnine with lime gave the pinewood reaction. At the end of the distillation, a most marked fæcal odour is observed ; and this is traced to the presence of skatole, as evidenced by analysis of the picrate, as also by the production of a yellow coloration when concentrated nitric acid is added to the aqueous solution, and the separation of a yellow, flocculent precipitate on addition of sodium nitrite. This result confirms the view that of the nitrogen-atoms in strychnine, the one forms part of a skatole or indole nucleus, the other of a hydride of a pyridine-derivative, probably methylpyridine. V. H. V.

Ecgonine. By W. Gintl and L. Storch (*Monatsh. Chem.*, **8**, 78—81).—A notice as to the directions in which the authors are working.

Bile Acids. By P. Latschinoff (*Ber.*, **20**, 1043—1053).—An examination of the products of oxidation of ox-gall yielded the following results :—Anhydrous cholic acid (if it is capable of existing) has the formula $C_{25}H_{42}O_5$; the hydrated cholic acid has the formula $C_{25}H_{42}O_5 + \frac{1}{4}H_2O$ when dried at 175°.

Anhydrous choleïc acid has the formula $C_{25}H_{42}O_4$; the hydrated acid dried at 175° has the formula $C_{25}H_{42}O_4 + \frac{1}{4}H_2O$. It contains two alcoholic hydroxyl-groups, and loses 4 atoms of hydrogen on conversion into dehydrocholeïc acid, $C_{25}H_{38}O_4$.

Mylius's desoxycholic acid (Abstr., 1886, 480) is identical with hydrated choleïc acid.

Cholic and choleïc anhydrides are obtained by heating the acids at 165°.

The proportion of choleïc to cholic acid in ox-gall is about 1 to 3·3 (comp. *Ber.*, **18**, 3043). N. H. M.

Crystalline Form of Choleïc Acid. By P. Latschinoff (*Ber.*, **20**, 1053—1056).—Anhydrous choleïc acid crystallises in the rhombic system (hemihedric), $a : b : c = 1 : 0{\cdot}5057 : 1{\cdot}85979$, a being the macro-axis, b the brachy-axis, and c the principal axis. The faces observed are 0P, $\breve{P}\infty$, $2\breve{P}\infty$, P, and $\infty\breve{P}\infty$.

Choleïc acid (with $1\frac{1}{2}$ mol. H_2O) crystallises in the quadratic system, $a : c = 1 : 2{\cdot}48282$ (c being the length of the principal axis). The crystals are a combination of three quadratic pyramids.

N. H. M.

Action of Oxidising Agents on Albumin from Eggs. By C. Wurster (*Ber.*, **20**, 1030—1033).—Fresh unfiltered albumin was treated with 1 per cent. sodium chloride solution and 1 per cent. lactic acid and shaken for 10 minutes; it was then mixed with hydrogen peroxide, placed in a eudiometer over mercury, and heated at 37—40° in an incubator. Coagulation generally took place without evolution of gas; oxygen was in all cases absorbed, although in small quantity. When the product, to which the name egg-caseïn is ascribed, is digested in the eudiometer with pepsin and hydrochloric acid at 37°, no change in the volume of the oxygen could be observed.

Egg-caseïn is readily soluble in dilute ammonia, and is precipitated on adding an acid. When treated with ammonia in presence of hydrogen peroxide, it is converted into a sparingly soluble, transparent, gelatinous substance. The latter dissolves slowly in aqueous soda. It has the property of completely precipitating aniline dyes from their solutions. When dried, it becomes horny and insoluble.

N. H. M.

Behaviour of Sodium Nitrite towards Albumin from Egg and the Colouring Matter of Blood. By C. Wurster (*Ber.*, **20**, 1033—1039).—Albumin is not affected by $\frac{1}{2}$ and 1 per cent. sodium nitrite solution at 37°. When the solution is made acid with lactic acid, it acquires a yellow colour, and coagulation takes place. When exposed to air in an incubator the colour darkens; when filtered and dried the precipitate becomes first orange-red, then fox-red.

The author showed previously that fresh blood does not decompose hydrogen peroxide in presence of lactic or acetic acids. The colouring matter of the blood is changed to a brownish-black substance, which is slowly decolorised by hydrogen peroxide, showing the various shades from dark-brown to white. No red colour is produced.

It is suggested that the colour of blonde and dark-brown hair may be due to the action of hydrogen peroxide on the colouring matter of the blood, whilst that of red and black hair is produced by the action of nitrous acid on the albumin and on the colouring matter of the blood respectively. The sudden becoming grey of

hair is accounted for by hydrogen peroxide being forced up into the hair, where it would give rise to an evolution of oxygen.

Observations made by the author on the formation of pigment in the skin under the influence of the sun are described.

N. H. M.

Physiological Chemistry.

Period required for Digestion in the Pig. By Ellenberger and Hofmeister (*Bied. Centr.*, 1887, 158—160).—The emptying of the stomach commences in 18 to 24 hours after feeding, and is completed in 36 hours, but a portion of the less digestible food generally remains in the large intestine, and may remain there for eight days; hence it is here that sparingly soluble poisons will be found. A portion of the meal remains in the stomach until the next meal is given, provided the period of time between the two meal times is not too lengthy, and then, if the meal is ample, all the residue of the former meal will be removed from the stomach, but if otherwise, a portion will remain. The first portions of the meal enter the small intestine within three hours, and in three hours more the cæcum is filled. The food remains but a short time in the smaller, whilst it remains a long time in the larger intestine. The reaction of the contents of the intestines is as follows:—Contents of the stomach, acid; only at the commencement of digestion and in the neighbourhood of the cardiac is it alkaline. The first portion of the small intestine (two-thirds or five-sixths) has an acid reaction, the remainder is alkaline; the contents of the duodenum are acid, the ileum (*Hüftdarm*) alkaline, and the jejunum variable. E. W. P.

Behaviour of the Three Isomeric Nitrobenzaldehydes in the Animal Body. By N. Sieber and A. Smirnow (*Monatsh. Chem.*, **8**, 88—93).—The experiments were made on dogs. 2 to 3 grams of each of the isomeric nitrobenzaldehydes were administered daily to dogs; this was continued for eight days, and then it was stopped for eight days, being given again at the end of that time. This treatment was continued for two months.

The results showed that all three nitrobenzaldehydes were oxidised in the organism to the corresponding nitrobenzoic acids, but were excreted in different forms. Paranitrobenzaldehyde is excreted as paranitrohippuric acid carbamide, metanitrobenzaldehyde as metanitrohippuric acid, and orthonitrobenzaldehyde as orthonitrobenzoic acid. G. H. M.

Therapeutic Action of Methylal. By A. Mairet and Combemale (*Compt. rend.*, **104**, 1022—1024).—The authors have administered methylal in a large number of cases of mental derangement of various kinds. The results were highly satisfactory except in the case

of alcoholic frenzy, and the commencement of simple insanity with nocturnal agitation. The dose required is 5 to 8 grams, and the effect is purely hypnotic. The action on the brain is transient, and there is no after-depression, and no interference with nutrition or any other functions.

The system somewhat rapidly becomes accustomed to the drug, which then ceases to produce any useful hypnotic effect, and in order to obtain the best results its administration must be discontinued for two or three days. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Decomposition of Carbonic Anhydride by Chlorophyll. By Pringsheim (*Bied. Centr.*, 1887, 168).—The author combats Regnard and Timiriazeff's conclusions drawn from their experiments on chlorophyll (Abstr., 1886, 254 and 266), but considers that it is not the chlorophyll colouring matter which decomposes carbonic anhydride, but a compound which by reduction of the anhydride is converted into chlorophyll. If the author is correct, then the absorption-bands of chlorophyll between B and C stand in no relation to the decomposition of carbonic anhydride, seeing that the compound which according to Timiriazeff decomposes carbonic anhydride does not show or produce these bands. E. W. P.

Physiological Rôle of Vine Leaves. By H. Mueller (*Ann. Agronom.*, **13**, 140).—A large number of leaf-bearing shoots should be sacrificed during the ripening of the fruit. These leaves require a large quantity of sugar for their development and for the support of their respiration. In removing the old leaves during the ripening of the fruit, too great a loss of assimilating tissues need not be feared, because the old leaves have only feeble assimilating power, and are moreover in the shadow of the upper leaves. The quantity of water contained in the leaves exercises a considerable influence on the amount of sugar they form. If two shoots are cut off and placed in darkness until all the starch has disappeared, then one of these simply placed in water, and the other injected with water under pressure, the latter will form starch much more abundantly than the former. The transformation of starch into sugar is similarly affected.

The vessels of climbing plants constitute important reserves of water, and in cultivating the vine as it is done in France these are lost. The vine cultivated in France also appears very inactive in habit, since the leaves do not commence the work of assimilation until June, whereas the American vines commence much earlier. Perhaps it is on this account they resist the phylloxera better.

J. M. H. M.

Is Nitric Acid Formed in the Organism of Higher Plants? By U. Kreusler (*Ber.*, **20**, 999—1001).—Potatoes were grown in saw-dust treated with a solution containing suitable nourishment free from nitrogen. The plant was then tested for nitrates with negative results. Hence it is concluded that the high percentage of nitrates found in the potato plant at certain times is not the product of any process connected with vegetation. N. H. M.

Intermolecular Respiration. By S. Jentys (*Ann. Agronom.*, **13**, 138).—Experiments on wheat, radish, and *Philadelphus coronarius* show that it is much easier to obtain intramolecular respiration in plants from amylaceous seeds than in those from oleaginous seeds; it takes place when the pressure of oxygen falls to 38 mm. When there is no oxygen, the first disengage much more carbonic anhydride than the second. Germinating seeds are much more sensitive to the diminution in the pressure of oxygen than older plants. With the buds of the *Philadelphus*, a very strong diminution in the oxygen pressure does not produce intramolecular respiration. The author admits with Detmer that it is the non-nitrogenous products of the decomposition of albuminoïds which give rise to both sorts of respiration. J. M. H. M.

True Nature of Starch Cellulose. By Griessmayer (*Bied. Centr.*, 1887, 190—192).—The investigation was undertaken to ascertain the true nature of the coating said to surround the true grains of starch (granulose). Meyer considers this coating not to consist of a compound present in the unaltered granule, but to be the result of change of the starch; this substance is obtainable by the action of acid, pepsin, &c., and is convertible into dextrin, and finally into saccharine compounds. This amylodextrin is with difficulty separated, unless it crystallises in spherocrystals; these crystals then react on polarised light in the same manner as starch grains, only that the dark cross is not orthagonal, but diagonal. The coatings can be obtained by the following method: 1000 grams of potato starch is allowed to remain for 100 days in 6 litres of 12 per cent. hydrochloric acid, the coatings are then separated and filtered off, and washed with water: when dried they weigh about 300 grams, and when boiled in water they dissolve almost entirely; there, however, remains a small portion of cellulose tissue, fat, &c.; from the solution, cold causes the dissolved compound to separate, forming spherocrystals of amylodextrin. E. W. P.

Sugars of the Soja Bean. By T. Morawski and J. Stingl (*Monatsh. Chem.*, **8**, 82—84; compare Abstract, 1886, 829).—The sugars, which occur in the soja bean to the extent of 12 per cent., were examined by precipitation with barium hydroxide and decomposition of the precipitate with carbonic anhydride. In this way, a light-coloured syrup was obtained, which was dissolved in 90 per cent. alcohol, and the solution fractionally precipitated with ether. Well-defined crystals of sucrose were obtained from the two last fractions with ether; this sugar was identified by polarisation before and after inversion. The uncrystallisable fractions contained sugars

which could not be identified with certainty; the rotatory power was higher than that of sucrose, and the sugars were more difficult to invert. The amount of sugar found, both by Fehling's solution and by polarisation, after inversion, was too small for the amount of sugar originally present. G. H. M.

Fat of the Soja Bean. By T. Morawski and J. Stingl (*Monatsh. Chem.*, **8**, 85—87; compare Abstract, 1883, 1024).—The authors conclude from the results of the "saponification value," the "iodine value," and the determination of the amount of free fatty acid, that the soja bean oil lies between marrow-seed oil and sesame oil. It most resembles the former. The sp. gr. of the fat is 0·9270 at 15°. G. H. M.

Russian Black Earth. By E. Brückner (*Bied. Centr.*, 1887, 148—149).—In many districts in West-South Russia soil is found containing a large percentage of humus (2 to 19 per cent.). Dokutschajef finds, as a rule, that this deposit consists of two layers; the upper, 0·5 m. thick, being homogeneous, fine-grained, and of a clayey consistency, and permeated by a thick network of grass roots; the lower layer of a similar character, but pierced with cavities and passages. No satisfactory explanation has as yet been given of the formation of this soil. E. W. P.

Value of the Phosphoric Acid in Thomas Slag. By M. Märcker (*Bied. Centr.*, 1887, 148—156).—Ground Thomas slag was compared with superphosphate and precipitated phosphates as manure for barley, oats, potatoes, and sugar-beet. The superphosphate yielded the highest results, and no difference in the composition of the crop as occasioned by the varieties of phosphate could be detected. On moorland soils, slag was found to surpass the other forms of phosphate, or at least to equal them. E. W. P.

Analytical Chemistry.

New Gas Burette. By B. Franke (*J. pr. Chem.* [2], **35**, 259—262).—The burette holds exactly 100 c.c., and is closed at one end by a small stopcock, at the other end by a wide bore stopcock leading into a wide tube holding some 50 c.c.; this serves to introduce the absorption reagent, and is closed by a stopper bearing a small stopcock. The sample of gas having been enclosed in the burette, the other half is completely filled with the absorption reagent, and the two well brought into contact by opening the wide bore stopcock and shaking; the reagent is then drained back into the reservoir, and ultimately poured out; the reservoir filled with water, and the whole being introduced into a cylinder of water, the large stopcock is opened, the pressure adjusted, and the volume read off. The apparatus is very simple and allows of very rapid estimations. H. B.

Burette Jet. By W. Leybold (*Zeit. anal. Chem.*, **26**, 230).—This jet, which requires no pinchcock, is closed at its upper end. A hole is blown in the side near that end, and the rough glass is filed away. The jet is thrust into the rubber tube so far that the hole is covered. The liquid is then delivered by squeezing up the rubber where it covers the hole. M. J. S.

Use of "Solid Bromine" for Decomposing Sulphuretted Minerals and Metallurgical Products. By A. Brand (*Zeit. anal. Chem.*, **26**, 222—226).—The article introduced into commerce by Franke as "*Bromum solidificatum*" consists of siliceous earth fritted together by means of a trace of alkali in the form of rods, and saturated with bromine. The rods of 7 mm. diameter contain about 1 gram; those of 15 mm. about 3 grams per centimetre. They afford a convenient and economical means of employing a definite quantity of bromine for any operation, especially as a substitute for chlorine in the attack of mineral sulphides, &c. The boat containing the substance is thrust into a tube connected with the bulbs for absorbing the volatile bromides; a sufficient number of the bromine rods are then inserted, and the tube is closed by a plug of plaster of Paris and a cork. The bromine is then driven over the heated substance by warming the rods. Sulphur, antimony, arsenic, and mercury are completely volatilised; copper, lead, nickel, cobalt, and silver remain in the boat; iron and zinc are incompletely driven over. A gram of substance can be completely decomposed in half an hour.

M. J. S.

Iodometric Studies. By G. Topf (*Zeit. anal. Chem.*, **26**, 137—217).—The addition of ammonium carbonate to solution of thiosulphate, recommended by Mohr as a means of preserving its strength, has no such effect, and moreover leads to serious errors in titrating iodine in a solution which is not acidified. Although ammonium carbonate has little effect on iodide of starch, yet with iodine it forms both iodate and hypoiodite, the latter of which immediately oxidises some of the thiosulphate to sulphate instead of to tetrathionate. The consequence is that less thiosulphate is required for decoloration, and although the addition of hydrochloric acid, after the disappearance of all the iodine, sets free that which had been converted into iodate, the results are still deficient by the amount consumed in forming sulphate. A series of titrations was made with thiosulphate solutions to which ammonium carbonates of various composition were added in the proportion of 2 and 5 grams per litre respectively. The deficiency in the quantity of iodine indicated was observed in every case, except in that in which, after the addition of the carbonate (2 grams per litre), carbonic anhydride was passed through the solution to produce ammonium hydrogen carbonate. The deficiency ranged from 3 to 20 per cent.; it increased with increase in the quantity of ammonium salt added, but diminished as that was more highly carbonated.

If an alkaline carbonate is present in a liquid, a little more iodine must be added to produce the blue colour with starch than would be the case in the absence of the alkali. On adding hydrochloric acid, all the missing iodine is recovered. The normal carbonates of the fixed

alkalis have a greater effect than that of normal ammonium carbonate, whilst the hydrogen carbonates of all the alkalis are practically without influence. Nevertheless even these, and other substances of very feeble alkalinity added to an iodine solution before titrating with thiosulphate, have an effect similar to that of ammonium carbonate on the thiosulphate solution, and to an extent far exceeding their retarding action on the formation of iodide of starch. With the hydroxides of sodium, barium, and calcium, the tendency is chiefly to the formation of iodate; nevertheless, as much as 34 per cent. of the iodine present has been observed to be consumed in the formation of sulphate. Dilution, or reduction of the proportion of alkali added, diminishes the total quantity of iodine absorbed, but increases the oxidation relatively to the formation of iodate. With the normal carbonates of sodium, potassium, and lithium, oxidation takes place to about the same extent as with the hydroxides, but there is less iodate formed. The hydrogen carbonates have a lower, but by no means insignificant action. It is entirely one of oxidation, no iodate being formed. With ammonia and normal ammonium carbonate, the tendency is chiefly to the formation of sulphate; the proportion of iodate rises with increased proportion of carbonic acid. The effect of ammonium hydrogen carbonate is far greater than that of the corresponding sodium and potassium salts.

Mixtures of alkaline carbonates with excess of barium, calcium, or zinc chloride, although neutral to phenolphthaleïn, still cause considerable oxidation to sulphate. Little or no iodate is formed. Zinc and magnesium hydroxides and magnesium carbonate cause both oxidation and formation of iodate. Aluminium hydroxide, on the contrary, has no action. An excess of alum added to ammonia produces a mixture which is entirely without influence on the titration of iodine. M. J. S.

Reaction of Thiosulphates. By F. A. Flückiger (*Chem. Centr.*, 1887, 362; compare this vol., p. 297).—The reduction of thiosulphates to sulphides by sodium, or by a mixture of zinc and iron filings in presence of soda, or by simple ignition, had been already published by the author in his "Pharmaceutical Chemistry."

M. J. S.

Zinc Determination. By M. Bragard (*Chem. Centr.*, 1887, 365).—Of the methods of precipitation as zinc sulphide, that with an alkaline sulphide, when Fresenius' precautions are attended to, gives the sharpest results, but the precipitate is troublesome to filter. Finkener's modification, in which the zinc is precipitated by hydrogen sulphide from a liquid very feebly acidified with sulphuric acid and largely diluted, yields a pulverulent precipitate which is easily washed. Precipitation from a formic or acetic acid solution gives good results, and is suitable for the separation of zinc from iron and nickel.

In the volumetric determination by sodium sulphide, ferric hydroxide may be used as an indicator. If test-papers are used those of lead and thallium exceed all others in sensitiveness. In determining volumetrically by potassium ferrocyanide with uranic nitrate as indi-

cator, a piece of filter-paper must be laid over the uranium paper so that only the clear liquid comes in contact with the latter.

M. J. S.

Detection and Estimation of Aluminium in Wine and Grapes. By L. L'Hote (*Compt. rend.*, **104**, 853—855).—250 c.c. of wine is evaporated to a syrup in a platinum dish, and mixed with pure sulphuric acid. The carbonised mass thus obtained burns readily to a white ash in a muffle. The ash is treated with 15 c.c. of nitric acid, mixed with 100 c.c. of a solution of ammonium molybdate in nitric acid (50 grams molybdic acid per litre), heated to boiling, the phosphomolybdic acid filtered off, and the iron and aluminium precipitated in the filtrate by ammonia and ammonium sulphide. The precipitate is roasted in presence of air, reduced in a current of hydrogen, and then heated in a current of hydrogen chloride, when the iron volatilises. The residue is treated with hydrofluoric and sulphuric acids to remove silica, strongly heated and weighed. It may be proved to be aluminium by heating it on charcoal with cobalt nitrate. A blank experiment is made with the same reagents and the aluminium found is deducted in each experiment.

Wines from seven localities were found to contain 0·012—0·036 gram of alumina per litre.

479 grams of red grapes gave 0·013 gram of alumina, whilst the stalks from which they had been stripped (6·482 grams) contained 0·003 gram.

C. H. B.

Detection and Estimation of Vanadium in Minerals. By L. L'Hote (*Compt. rend.*, **104**, 990—992).—The substance (4 parts) is intimately mixed with carbon (1 part) and heated at 250° in a current of chlorine in a tube connected with a condensing apparatus consisting of several bulbs containing distilled water. If the substance contains arsenic, it should first be roasted in presence of air. The presence of vanadium is indicated by the formation of a red coloration, due to vanadic acid in the first bulb. If the quantity is too small to be recognised in this way, the contents of the bulbs are dissolved in dilute hydrochloric acid, evaporated to dryness, and moistened with *colourless* ammonium sulphide, when the characteristic colour of vanadium sulphide becomes visible.

Small quantities of vanadic acid can be estimated by Margueritte's method for the estimation of small quantities of iron. A standard solution of vanadium is prepared by dissolving vanadic anhydride in sulphuric acid; 1 c.c. of this solution = 0·00028 gram of vanadium. The solutions can be reduced with zinc and titrated with very dilute permanganate solution, care being taken to use distilled water which has no action on the permanganate.

If the proportion of vanadium in the mineral is considerable, the contents of the first bulb will be greenish-blue, and when evaporated with ammonia and heated to redness vanadic anhydride is left, and can be weighed.

By this method, the author has detected vanadium in two specimens of bauxite, two specimens of pitchblende, a hydrated ferric oxide, and basic Bessemer slag.

C. H. B.

Estimation of Vanadic Acid. By A. Ditte (*Compt. rend.*, **104**, 982—987).—When ammonium vanadate is precipitated in presence of ammonium chloride and washed with a solution of this salt as in Berzelius' method, it is necessary to remove the ammonium chloride adhering to the precipitate, since it would partially reduce the latter on heating. If strong alcohol is used for this purpose, the ammonium chloride is precipitated in the filter, and is only dissolved with difficulty, whilst if dilute alcohol is employed, small quantities of the vanadate are dissolved. The following method avoids these difficulties.

When the vanadic acid is present in the form of a pure alkaline salt, the solution, if not already neutral or alkaline, is mixed with ammonia and heated until colourless. The solution is cooled to 30—40°, mixed with powdered ammonium chloride until nearly saturated, then with four or five volumes of alcohol, and allowed to remain. If the solution is saturated with the ammonium chloride at a temperature not exceeding 40°, the alcohol precipitates only a small quantity of the salt, and this readily dissolves during washing. Care should be taken to avoid rubbing the sides of the vessel. The precipitate is collected and washed with alcohol.

If the solution contains salts which are only slightly soluble in alcohol, it is mixed with a slight excess of solid ammonium chloride, then with 4 or 5 vols. of a saturated solution of this salt, and allowed to remain for several hours. The clear liquid is decanted off through a filter, and the precipitate mixed with a fresh quantity of ammonium chloride solution, care being taken that a small quantity of the undissolved solid is always present. After remaining for some hours, the liquid is again decanted off, and this treatment is repeated two or three times according to circumstances. The filter is then washed with hot water to dissolve the adhering precipitate, and the solution is allowed to run into the beaker containing the bulk of the precipitate, which is partially dissolved, and the liquid now contains ammonium vanadate partly in solution, partly precipitated, but free from other salts. It is treated in the manner described above.

The washed ammonium vanadate is dried and heated in a platinum capsule until the filter burns, and is then kept in fusion until the precipitate is completely oxidised. In order to prevent the formation of V_2O_4,V_2O_5, the partially roasted precipitate is moistened with nitric acid, dried, and then fused.

When the vanadic acid is not present in combination with an alkali, the other metallic oxides must be removed by suitable methods, and the vanadic acid converted into an alkaline salt. C. H. B.

Determination of Nitrates in Well Waters. By L. Spiegel (*Chem. Centr.*, 1887, 363—364).—Wagner's chromic oxide method (this Journal, 1871, 753) did not give satisfactory results. The most accurate is the Schulze-Tiemann method (this Journal, 1873, 529, and 1874, 91), but it is necessary that the end of the gas delivery tube should be plunged deep in the soda solution, that boiled ferrous chloride and hydrochloric acid should be used, and that the last traces of nitric oxide should be driven over into the measuring tube by

carbonic anhydride. Of the methods depending on reduction to ammonia, that of Harcourt and Siewert with König's modifications is the most suitable. Heating over the free flame, however, inevitably causes potash to be carried over.

Good results can be obtained by the Marx-Trommsdorf indigo process, if the nitrate solution used in standardising is of approximately the same strength as that to be tested. Nitrites have, for the same quantity of available oxygen, the same oxidising power as nitrates. Both of these methods are vitiated by organic matter.

A colorimetric process based on the blue coloration with diphenylamine in strong sulphuric acid gives a fairly accurate determination very readily. At least 9 volumes of sulphuric acid must be used for 1 volume of water. Organic matter is without influence, but ferric salts produce a blue colour by themselves and must be removed. M. J. S.

Detection of Cane-sugar, Glucose, and Dextrin in Wines. By Tony-Garcin (*Compt. rend.*, **104**, 1002—1003).—The wine is decolorised by means of animal charcoal, and its rotatory power and reducing power are determined.

When the reducing power is equivalent to 2 grams or less, and the rotatory power is more than $+13'$, the wine contains some foreign dextrogyrate substance. If the wine contains more than 2 grams of reducing matter per litre, 1·5 gram is deducted, and the remainder is multiplied by 6 and distinguished by the sign +. This is added algebraically to the observed rotatory power expressed in minutes, and if the sum is greater than $+13'$, the wine probably contains foreign dextrogyrate substances, and this conclusion is certain if the excess above $+13'$ is equal to $10'$.

The nature of the foreign matter is determined by chemical methods; cane-sugar by inversion, dextrin by saccharification; glucose, in the absence of cane-sugar and dextrin, by the relation between the reducing action and rotatory power of the wine.

When polarimeters other than Laurent's are used, it may be taken that the rotatory power of wines free from foreign dextrogyrate matter is never more than $+13'$. C. H. B.

New Test for Coniferin. By H. Molisch (*Chem. Centr.*, 1887, 366).—An alcoholic 20 per cent. solution of thymol is diluted with water as long as it remains clear; an excess of solid potassium chlorate is added and after some hours the mixture is filtered. Coniferin, treated with a drop of this solution and two drops of strong sulphuric acid, acquires a fine blue colour when evaporated in direct sunlight. A wood section, or wood-pulp paper moistened with this solution, and a drop of hydrochloric acid rapidly becomes blue even in the dark. Since coniferin is only present in lignefied cell-walls, thymol may probably be of use in the microscopic detection of wood-fibre. M. J. S.

General and Physical Chemistry.

Absorption-bands of Chlorophyll. By F. Stenger (*Ann. Agronom.*, **13**, 175—176).—Reinke has maintained that the dark bands in the absorption spectrum of chlorophyll do not correspond with the maximum absorption of light, but that some of them are mere effects of contrast, subjective impressions due to the eye itself. The present memoir is directed against this conclusion. J. M. H. M.

Electromotive Force produced by Light in Selenium and the Consequent After-action. By S. Kalischer (*Ann. Phys. Chem.* [2], **31**, 101—108).—About the same time that Bell discovered that an intermittent exposure to light generated a current in selenium which affected the telephone, the author met with a selenium cell which under the action of light produced a current which could be detected by a galvanometer. As it appeared that those who have paid special attention to the preparation of selenium cells have seldom met with cells which were so sensitive to light, an attempt was made in the first place to discover the proper mode of making such cells.

The cell consisted of two parallel wires wound round a stem, with selenium melted between them. In order to ensure the sensitiveness of the cell to light, it was heated to 190—195°, kept at this temperature for half an hour, and then allowed to cool for an hour. If at first not successful, a repetition of the process produced the desired result.

When such a cell is inserted in a galvanometer circuit and exposed to the action of light, there is a permanent deflection. It is found that the cells which are sensitive have a large specific resistance. To produce a current in general, a very intense source of light is necessary. The sensitiveness, and with it the specific resistance, were found in many cases to diminish with the time. The author believes that these facts are very well explained by the hypothesis advanced by Siemens that there is a metallic modification of selenium.

Again, if a cell is placed in an arm of a Wheatstone's bridge and the balance obtained in the usual manner, on allowing light to fall for an instant on the cell, there is a deflection, but the mirror does not return to its position of rest at once, and gradually creeps up to a fixed position. This is not due to the effect of heat, for it occurs even when the cell is shielded by an alum cell, or by a current of water circulating round it.

It is proposed to call this phenomenon after-action (*Nachwirkung*), from the analogy it presents to other well-known physical facts. The analogy is traced out by showing that the after-action is dependent on the duration and the intensity of the illumination of the cell. It is also shown to be independent of the direction of the current.

C. S.

Density of Liquid Methane and of Liquefied Oxygen and Nitrogen. By K. Olszewski (*Ann. Phys. Chem.* [2], 31, 58—74).—In some previous experiments, the author had determined the densities of liquefied gases at varying temperatures and pressures. It was impossible to compare the results with each other, because of the large coefficient of expansion of a liquefied gas and the very considerable alteration of volume by pressure. A determination of the densities at a common pressure, namely, the pressure of the atmosphere, and at the corresponding temperature of the boiling points, was attempted.

The chief part of the apparatus was a glass tube, into which the gas was condensed. This tube was very carefully annealed by heating it in anhydrous magnesia and allowing it to cool very gradually, a process which fitted it to withstand great changes of temperature and severe pressure.

Ethylene was made to circulate through a copper spiral, surrounded by a freezing mixture of carbonic anhydride and ether, contained in a vessel which was exhausted. Thus a large quantity of ethylene was rendered liquid, and passed into a vessel surrounding the condensing tube. When this vessel was exhausted so that the pressure sank to a few millimetres of mercury, the temperature of the ethylene fell so much that the gas in the tube was liquefied. The temperature of the boiling point had first to be measured. For this purpose about 12 to 15 c.c. of liquid gas was produced as already described under pressure, and after a time the pressure was gradually diminished to atmospheric pressure. The liquid was then gently boiled, and after a short time evaporation went on at the surface alone until the whole was vaporised. As this took about 5 to 15 minutes, there was ample time to take the temperature of the boiling point. This was determined by means of a hydrogen thermometer; a comparison instituted to compare the indications of thermometers filled with other gases showed that for the temperatures recorded the readings did not differ by more than about 1°.

To determine the density of the liquefied gas, it was condensed into the glass tube which had been calibrated, so that its volume was easily read off from a millimetre scale. The pressure being lowered to atmospheric pressure, the liquefied gas vaporised, and the amount of vapour produced was found from the volume of water displaced in an aspirator. Thus with the known readings of the barometer and thermometer the weight of the liquefied gas was determined, and from it the density.

The mean results of the experiments are given in the table:—

Substance.	Pressure.	Temp.	Density.
Methane	736·6 mm.	−164·0°	0·415
Oxygen	742·1 „	−181·4	1·124
Nitrogen	742·1 „	−194·4	0·885

C. S.

Vapour-density Apparatus. By T. T. P. B. Warren (*Chem. News*, **55**, 228).—A modification of Victor Meyer's tube.

Determination of Vapour-densities. By C. Schall (*Ber.*, **20**, 1435—1441).—A Jolly's air thermometer modified for vapour-density determination is described with sketch; results obtained by means of the apparatus are given. The author recommends the method for substances with high boiling points; it has the advantage over the methods of Habermann and La Coste, in not requiring such large amounts of substance or capacious apparatus for heating.

N. H. M.

Expansion and Compressibility of Water: Displacement of the Point of Maximum Density by Pressure. By E. H. Amagat (*Compt. rend.*, **104**, 1159—1161).—The apparatus was so arranged that the water was always brought to the same volume at the particular temperatures, the pressure required being measured. If the same pressure is necessary at two different temperatures, it is evident that the point of maximum density lies between them. The effect of the alteration in the volume of the piezometer is eliminated, since it must be the same in both cases. The pressures employed exceeded 3200 atmos., and the temperature varied from 0—50°.

Under a pressure of 200 atmos., the point of maximum density is very near 0°, and seems to lie between 0° and 0·5°. At 700 atmos., it is below 0°.

If the phenomena at each temperature are represented by a curve with the pressures for abscissæ and the volumes for ordinates, the series of curves represent the volumes occupied by the same mass of water at different temperatures and pressures. These curves intersect at points which correspond with changes in the sign of the dilatation of the water, and as the pressure increases they arrange themselves successively in the order of the temperatures. At 200 atmos. they are normal, and are closer together the lower the temperature. As the pressure increases, the coefficient of expansion increases, at first rapidly, and afterwards more slowly, contrary to the phenomenon observed with all other liquids. At about 3000 atmos., the coefficient of expansion ceases to increase, and probably at still higher pressures it diminishes, like that of all other liquids. For equal pressures, the effect is less marked the higher the temperature.

Between two given pressures, the compressibility diminishes as the temperature rises, as previously observed by Grassi, a behaviour contrary to that of all other liquids. This result is a natural consequence of the disappearance of the point of maximum density. For the same reason, diminution in the coefficient of compressibility disappears as the pressure increases, and it also disappears with elevation of temperature, as Pagliani and Vicentini have observed. The temperature at which the inversion takes place is lower the higher the pressure.

A sufficiently high pressure brings water into the category of ordinary liquids; at about 3000 atmos., the last traces of perturbation of the ordinary laws, resulting from the existence of a point of maximum density, disappears.

No other liquid hitherto examined by the author has shown any signs of a point of maximum density under any pressure.

C. H. B.

Compressibility of Aqueous Solutions of Chlorides. By M. Schumann (*Ann. Phys. Chem.* [2], **31**, 14—58).—Four very sensitive piezometers were used. The compressibility, μ, was determined from the formula—

$$\mu = \frac{\Delta v}{v}\frac{760}{p} + K,$$

where v is the volume of the solution, and Δv the change of volume produced by pressure p. p was measured by a mercury manometer, v by weighing the piezometer filled with distilled water, Δv by calibrating the capillary tube attached to the instrument. K, as Regnault and Grassi pointed out, is a constant which must be determined for each particular instrument by subtracting the apparent compressibility of water as observed in it from the value of the true compressibility given by Regnault.

Experiments were made with four or five solutions of different strengths of ammonium, barium, potassium, strontium, calcium, and sodium chlorides at two different temperatures, so that the temperature coefficient of compressibility could be found for the purpose of reducing all the results to one common temperature for the sake of comparison.

The general results of the paper are :—The compressibility of water is considerably altered by the addition of the chlorides, and in a different degree for each chloride. The compressibility of a solution diminishes as the strength increases. As regards the effect of temperature, all weak solutions have a greater compressibility at 0° than at higher temperatures, as in the case of water; in the case of ammonium and calcium chlorides, and seemingly of potassium chloride, this is true for all degrees of concentration. For sodium and strontium chlorides, after a certain strength of solution is reached, the influence of temperature is independent of the strength of the solution.

The results of the experiments are recorded in numerous tables, and the values obtained for the compressibility of the several solutions appear to agree well with the other determinations that have been made, especially with those of Röntgen and Schneider (*Ann. Phys. Chem.* [2], **29**, 165).

The conclusion of the paper is occupied in tracing the connection between the compressibility of the solutions and the equivalent weights of the salts dissolved. The relation between the pressure required to produce the same change of volume as is caused by the solution of the salt, and the amount of salt dissolved, is investigated.

C. S.

Rate and Vapour-tension of Disscciation. By W. Müller-Erzbach (*Ann. Phys. Chem.* [2], **31**, 75—78).—The present paper is a reply to some objections which have been made by Lescœur against the author's method of determining the vapour-tension of dissociation. Lescœur (this vol., p. 100) states that the rate of dissociation is a

function of the state of the body as well as of the tension, and on this ground considers Müller-Erzbach's formula to be erroneous.

On the other hand, it is pointed out that in the case of hydrated solutions, the author's method gives results in accordance with those which have been obtained by others from the barometric method. In the case of salts containing water of crystallisation, he finds that within wide limits the tension is independent of the weight of the substance employed and the dimensions of the tubes containing it. During the melting of sodium hydrogen phosphate, the vapour-tension remained constant. Finally he asserts that in many cases the barometric method is very unsatisfactory, because, especially after heating, the values of the tension are often too great, whereas his own method gave constant results for considerable periods of time.

C. S.

Effect of Pressure on the Decomposition of Dissolved Chlorides. By G. Foussereau (*Compt. rend.*, **104**, 1161—1163).—The method previously employed to determine the degree of alteration of chlorides in aqueous solution (Abstr., 1886, 844, 975), has been used to investigate the effect of pressure on the rate and extent of the change. A variation of about 1 atmo. produces no sensible effect. A pressure of 175 atmos. causes a reduction of about 1 per cent. in the resistance of a dilute solution of ferric chloride, which indicates that the decomposition is increased by pressure. After removal of the pressure, the resistance of the liquid gradually resumes its normal value. The effect of pressure on very dilute solutions cannot be very great, since the dissociation is almost complete under ordinary pressure. With a stronger solution of ferric chloride, a pressure of 175 atmos. produces a diminution in the resistance amounting to nearly 5 per cent., and hence it is evident that with stronger solutions the effect of pressure is much greater. When the pressure is removed, the resistance gradually returns to the normal value.

A solution of aluminium chloride shows similar phenomena in a lower degree. C. H. B.

Velocity of Chemical Reactions. By F. Urech (*Ber.*, **20**, 1634—1636).—This paper is an explanation of a criticism of Reicher on the author's statement that in any reaction between two substances, A and B, the velocity of the reaction is affected in different degrees by the presence in excess of A, or of its equivalent of B. On the other hand, the investigations of Reicher on saponification have shown that the presence on the one hand of excess of alkali, and on the other of excess of ethereal salt, does not affect the value of the specific velocity.

It is here shown that in the differential equation $\frac{-dt}{dC} = \frac{1}{K_1 C.C_1^2}$ C cannot be taken as either greater or less than C_1 without alteration of the value for K, inasmuch as C is altered to the first, and C_1 to the second power. The excess of one or other of the ingredients beyond that of the equivalent proportion must be considered as accelerating the change, and such an excess can in no wise be regarded as so much chemically inert matter. V. H. V.

Demonstration of Avogadro's Hypothesis. By C. Schall (*Ber.*, **20**, 1433—1435).—A balance provided with a combined scale is employed, to which large light vessels of as nearly equal capacity as possible are suspended. By means of the scale, which is described, the deviation produced in the index needle can be converted into a number expressing the density. N. H. M.

Practical Thermo-regulator. By L. Rugheimer (*Ber.*, **20**, 1280—1284).—A modification of an air-mercury regulator, which presents no specially novel point of construction. The results of thermometer readings show a variation of $\pm$ 0·5°. V. H. V.

Inorganic Chemistry.

Perbromic Acid. By R. W. E. MacIvor (*Chem. News*, **55**, 203).—Bromine is without action on hydrated perchloric acid, anhydrous perchloric acid, and perbromate of silver, even when the substances are heated together in closed tubes. R. R.

Diamidogen or Hydrazine. By T. Curtius (*Ber.*, **20**, 1632—1634).—See p. 715.

Nitrous Acid. By E. Drechsel (*Ber.*, **20**, 1456—1457).—When Fehling's solution is added to a solution of sodium nitrite, no reduction takes place; on treating the boiling solution with dilute sulphuric acid and then adding caustic soda until alkaline, a reduction takes place with formation of a yellow or red precipitate of cuprous oxide. The reduction is also produced by passing nitrous anhydride through Fehling's solution, but much more slowly than in the above reaction. It is suggested that in the reaction with sodium nitrite and sulphuric acid the reduction is due to the formation of hydroxylamine and nitric acid. N. H. M.

Hydrates of Sodium Arsenate. By H. Lescœur (*Compt. rend.*, **104**, 1171—1174).—The percentage of water in commercial sodium arsenate varies from 43·65 to 57·45, and the published statements as to the proportion of water normally present in the crystals are very conflicting.

Measurements of the vapour-pressure of crystallised disodium hydrogen arsenate indicate the existence of two definite hydrates only, $Na_2HAsO_4 + 12H_2O$ and $Na_2HAsO_4 + 7H_2O$. The first is not very well defined, and its vapour-pressure is practically identical with that of a saturated solution of the salt. It effloresces in dry air at 20°, and forms the second hydrate. The heptahydrate is stable in dry air, but in a moist atmosphere it gradually absorbs water until it approximates in composition to the higher hydrate. If crystallisation

takes place above 23°, the heptahydrate only is formed, but if this is left in the mother-liquor, or is exposed to moist air, it is more or less completely converted into the duodecahydrate.

In preparing the arsenate, a product of constant composition can only be obtained by drying the finely-powdered crystals in air at the ordinary temperature. C. H. B.

Particular Case of the Formation of Sodium Hydrogen Carbonate. By P. de Mondésir (*Compt. rend.*, **104**, 1102).—Normal sodium carbonate containing 1 mol. H_2O absorbs carbonic anhydride very slowly if at all at the ordinary temperature. If, however, it is mixed with a small proportion of the hydrogen carbonate the reaction commences immediately, and proceeds with a velocity which depends on the proportion of acid carbonate present and the perfection of admixture of the two salts. C. H. B.

Solubility of Lithium Carbonate. By C. N. Draper (*Chem. News*, **55**, 169).—The author finds that the solubility of lithium carbonate at 15° is 1·4787 per cent., or nearly half as much again as that usually given; and at 100° it is 0·7162 per cent.

R. R.

Argentous Compounds. By E. Drechsel (*Ber.*, **20**, 1455).—When an ammoniacal silver solution is kept for some time in contact with peptone, it gradually acquires a deep port wine colour like that of so-called argentous oxide; when a current of ozonised air is passed through the solution, it becomes colourless without precipitation. This reaction is most readily explained on the assumption that the red solution contains argentous oxide. On the other hand, it is conceivable that silver peroxide was formed from the silver, and that this reacted with the ammonia present with formation of silver oxide and evolution of nitrogen. N. H. M.

The Lowest Compounds of Silver. By O. v. d. Pfordten (*Ber.*, **20**, 1458—1474; compare Abstr., 1885, 955).—20 c.c. of a 12·5 per cent. solution of sodium tartrate, and a solution of 2 grams of silver nitrate, are mixed with 1½ litres of water; 2 c.c. of a 4 per cent. solution of sodium hydroxide is then added, the whole being stirred violently. After five hours, the supernatant liquid is poured off from the fine, black precipitate. The solution is treated in like manner three times with the same result. The united products of several experiments are washed by decantation with a dilute solution of sodium sulphate; water alone cannot be used. The purified black compound is probably argentous tartrate.

When a solution of 10 grams of silver nitrate in 20 c.c. of water, in presence of sufficient ammonia to give a clear solution, is gradually treated with 4 c.c. of a concentrated solution of phosphorous acid, a black precipitate is formed. The solution is filtered, and again treated in the same way with phosphorous acid. The black compound is washed with water until the filtrate comes through turbid, and then with ammonia.

Argentous oxide, Ag_4O, is prepared by treating either of the above black salts with alkali, and washing with water containing alkali. It forms a deep black, amorphous substance; it must be kept under dilute alkali. It cannot be dried without decomposition; water decomposes it. When treated with a mixture of potassium permanganate and sulphuric acid, it dissolves as an argentic salt. By means of this reaction, the formula of the compound was established; the wet substance was added to a mixture of titrated permanganate solution and dilute sulphuric acid, and the permanganate titrated back with a solution of ferrous ammonium sulphate; the silver was determined in the same solution, and the relative amounts of silver and of oxygen used up determined.

Argentous oxide is insoluble in ammonia and in acetic acid; it is converted by hydrochloric acid into a mixture of silver and silver chloride. Phosphorous and sulphurous acids do not dissolve it. Hydrogen peroxide has no action on it in the cold; when warmed, metallic silver is formed. Alcohol reduces it slowly. Mercury has no action on it. It is somewhat soluble in water; the solution is greenish, reacts neutral, and is not precipitated by soda solution or by hydrochloric acid. Sulphuric acid decomposes it with formation of silver and evolution of oxygen; the same result is produced but more slowly by hydrocyanic acid, by sodium chloride, and other indifferent solutions.

Argentous sulphide, Ag_4S, is prepared from the black argentous salts by the action of sodium hydrogen sulphide; it is a black, amorphous compound; when dried it is grey. Water decomposes it after a short time. It is insoluble in ammonia, dissolves sparingly in warm dilute nitric acid, decomposes with separation of sulphur when treated with strong nitric and sulphuric acids. It dissolves in hydrochloric acid, and is precipitated unchanged by water; it is also soluble in potassium cyanide solution (dilute sulphuric acid gives a black precipitate). Potassium permanganate and sulphuric acid dissolve it with separation of silver. When dried, or when kept under pure water, it changes into a mixture of silver (2 mols.) and silver sulphide (1 mol.). (Compare also Trans., 1887, 416.)

N. H. M.

Specific Gravity of Lime-water. By J. A. Wanklyn (*Chem. News*, **55**, 217).—The author's determination of the specific gravity (1002·35) of lime-water containing 1·344 grams of calcium oxide per litre, shows that when 1·344 grams of lime was dissolved in 1001 c.c. of water, the substances contracted to 1 litre. R. R.

Action of Ammonia on Bleaching Powder; Constitution of Bleaching Powder. By G. Lunge and R. Schoch (*Ber.*, **20**, 1474—1482).—When bleaching powder is treated with aqueous ammonia, 34·76 to 36·06 per cent. of lime is dissolved. When ammonia mixed with alcohol (Dreyfus, Abstr., 1885, 19) is used, the amount dissolved is rather less. The gas given off was examined, and found to consist of nitrogen, together with a small quantity (less than 3 per cent.) of oxygen and carbonic anhydride. These and further experiments,

showing the actual amount of nitrogen evolved in relation to the amount of bleaching powder employed, confirm the correctness of the equation suggested by Kolb (*Ann. Chim. Phys.* [4], **12**, 269).

The results of seven experiments, in which chloride of lime was heated at its melting point, gave 5·24 to 6·08 per cent. of oxygen, 0·58 to 1·12 per cent. chlorine as hypochlorous acid, and 3·69 to 6·18 per cent. of free chlorine. The equation given by Dreyfus (*loc. cit.*), which requires 10·53 per cent. of chlorine and 7·1 per cent. of oxygen, is therefore incorrect. N. H. M.

Barium Phosphates; their Application in Acidimetry. By A. Villiers (*Compt. rend.*, **104**, 1103—1106).—Phosphoric acid is bibasic when phenolphthaleïn is used as an indicator, and can be titrated with a solution of potassium or barium hydroxides. Other free acids, such as hydrochloric, sulphuric, acetic, can be titrated in presence of phosphoric acid by means of potassium hydroxide, but not with baryta.

Joly has already shown that when barium chloride is added to disodium phosphate the solution becomes acid, but the author gives a somewhat different explanation of the phenomenon.

If the acid solution produced by mixing solutions of disodium phosphate and barium chloride is mixed with phenolphthaleïn, and then with baryta solution, the addition of the first few drops of the alkali causes a somewhat rapid appearance of the red colour, but after five or six minutes this disappears, and a somewhat considerable quantity of baryta is necessary for the production of a persistent coloration. The volume of baryta solution required to produce the second end reaction varies with the proportions of barium chloride and disodium phosphate.

In presence of a large excess of disodium phosphate, the precipitate after washing and drying at 120—130° is constant in composition; it is barium sodium phosphate, $BaNaPO_4$. Its formation takes place in two stages, the first of which is represented by the equation $Na_2HPO_4 + BaCl_2 = BaHPO_4 + 2NaCl$. The acidity of the liquid at this stage is due to the formation of a small quantity of tribarium phosphate, and the consequent liberation of free acid. In the second stage, the barium hydroxide acts on the barium hydrogen phosphate in presence of sodium chloride, with formation of barium chloride, water, and barium sodium phosphate.

Barium sodium phosphate has previously been obtained in hydrated crystals by Schulten by the action of sodium phosphate on sodium silicate and barium hydroxide (Abstr., 1883, 711). It can also be prepared in an amorphous and less pure condition by the action of barium hydroxide on a solution of disodium phosphate, and in small quantity by adding barium chloride to a solution of trisodium phosphate, but it can only be obtained in a state of purity by the method described above.

Tribarium phosphate is obtained only by pouring sodium phosphate into a solution containing a large excess of baryta.

Barium hydrogen phosphate which has been precipitated for some time, and has become crystalline, is not readily converted into the

double phosphate, a proof of the alteration which the precipitate undergoes in course of time.

From these facts, it is evident that free acids cannot be accurately titrated by means of baryta in presence of disodium phosphate, and this is true also of the titration of phosphoric acid in presence of alkaline salts. Accurate estimations can, however, be made in either case by means of potassium hydroxide solution. C. H. B.

Thallium in Platinum. By H. N. Warren (*Chem. News*, **55**, 241).—The author detected thallium in platinum wire and foil spectroscopically. Ten grams of the wire was dissolved in aqua-regia, evaporated to dryness, redissolved, slightly acidified with nitric acid, and hydriodic acid added to precipitate the thallium as thallic iodide; the precipitate was washed with alcohol, dried, and weighed. From 0·02 to 0·1 per cent. thallium was found, the wire containing larger amounts than the foil. Traces of thallium were obtained from several samples of platinum ore, and alloys of platinum with thallium were found to be useless for wire when 0·5 of the latter metal was present, whilst 2 per cent. caused the metal to become fusible at a red heat. R. R.

Preparation of Anhydrous Metallic Chlorides. By H. N. Warren (*Chem. News*, **55**, 192).—The metallic oxide, such as aluminium oxide, is heated to redness in a large tubulated earthenware retort into which the vapour of petroleum previously saturated with hydrochloric acid gas, or with chlorine, is distilled. Fumes of the chloride are at once evolved, and may be condensed in a receiver. R. R.

Action of Nitrogen on certain Metals. By H. N. Warren (*Chem. News*, **55**, 155).—Bars of iron, copper, nickel, cobalt, &c., maintained at a bright red heat for some hours in an atmosphere of dry ammonia, and then allowed to cool in the same, were found to exhibit crystalline surfaces and fractures together with great brittleness. These effects were found to be proportionate to the quantity of nitrogen contained in the metal, and this increased up to a certain point with the duration of the heating. Thus a bar of iron heated in ammonia for two hours yielded 0·004 per cent. of nitrogen; a similar one after four hours' heating contained 0·01 per cent.; and others after 10 or 12 hours' heating gave 0·5 per cent. These last were so brittle that they broke on falling from a height of 6 feet. Some of the copper bars that were brought into the air before they were quite cold, spontaneously split with some violence in a transverse direction. When anhydrous ferrous chloride was substituted for the iron bar, a silvery, spongy mass of iron nitride was obtained containing 4 per cent. of nitrogen. An amorphous, green powder of copper nitride was formed by gently heating cupric oxide in ammonia gas; this decomposed with violence at a dull red heat into copper and nitrogen gas. When mercuric oxide is similarly treated, the like reaction occurs, but at a temperature of 205° the compound formed explodes with fearful violence. R. R.

Action of Ferric Sulphate on Iron. By A. E. Menke (*Amer. Chem. J.*, **9**, 90—93).—The action increases approximately with the amount of ferric sulphate, whether at a boiling temperature or in sealed tubes at 110°. The addition of the theoretical amount of sodium or potassium carbonate necessary for the precipitation of the iron salt reduces the action to about one-third, but calcium carbonate has no effect, or not so much; the action is less on steel than on boiler plate. H. B.

Titanium Carbide in Pig-iron. By P. W. Shimer (*Chem. News*, **55**, 156—158).—From the residue left on dissolving 250 grams of pig-iron in dilute hydrochloric acid, the author separated about 1 gram of a material consisting largely of minute, cubical, metallic crystals. Analysis showed that 88 per cent. of this material was composed of titanium and carbon very nearly in atomic proportions; the crystals are therefore regarded as a titanium carbide, TiC. The five or six pig-irons examined all contained these crystals, and a sample of No. 1 Barrow foundry iron yielded 0·203 per cent. of titanium.

In separating the titaniferous material from the graphite, &c., in the residue, a very slightly inclined plane, 12 feet long and 5 inches wide, made of window glass, was made use of. The material was placed at the upper end, and water allowed to drip upon it slowly, by which the lighter particles were carried forward faster than the heavier crystals. R. R.

Formation of Complex Inorganic Acids. By E. Drechsel (*Ber.*, **20**, 1452—1455).—Silicotungstic acid can be readily prepared as follows:—Pure sodium tungstate is dissolved in a little boiling water, almost neutralised with nitric acid, and filtered. The crystals are washed with cold water, dissolved in water, and boiled with gelatinous silica until the solution no longer gives a precipitate with hydrochloric acid. It is filtered, evaporated, treated when cold with a large excess of sulphuric acid previously diluted with an equal volume of water, and allowed to cool. Ether is then gradually added, when the liquid becomes turbid and separates into three layers—the lowest oily and containing most of the silicotungstic acid; the middle layer an aqueous solution of hydrogen sodium sulphate and sulphuric acid; the upper layer ether. The lowest layer is separated, freed from ether by evaporating on a water-bath (avoiding too high a temperature), and allowed to cool. The acid separates in splendid crystals.

When a concentrated aqueous solution of phosphotungstic acid is treated with an equal volume of ether, oily drops form at the surface of contact of the water and ether, and then sink, forming a third layer; the latter has the sp. gr. = 1·525. Crystallised phosphotungstic acid dissolved in the smallest amount of ether gives an oil, sp. gr. = 2·083.

Phosphotungstic acid is prepared by dissolving 500 grams of pure sodium tungstate and 250 grams of crystallised sodium phosphate in 500 c.c. of water and evaporating until a skin is formed on the surface. 700 to 800 c.c. of hydrochloric acid (sp. gr. = 1·14) is added to the boiling solution, which is again evaporated and allowed to cool. The

whole is gradually treated with pure ether, being well shaken all the time, until a layer is formed above the acid solution. It is then left until the lower layer is clear, separated and treated with an equal volume of water; the ether is then evaporated; if the solution becomes bluish, chlorine water is added. It is evaporated to dryness, dissolved in hot water; on cooling the acid separates in splendid crystals.

Phosphomolybdic acid is prepared in a similar manner.

N. H. M.

Equivalent and Atomic Weight of Thorium. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 1665—1676).—The accepted value for the atomic weight of thorium is 232·4, which is in accordance with the determinations of its specific heat.

In this paper, determinations are given of the equivalent of thorium and of the molecular weight of the chloride, and from these values, together with considerations of the position of the metal in the periodic system, the atomic weight is deduced.

The thorium oxide is prepared from the mixed sulphates obtained by dissolving thorite in sulphuric acid; from this solution, the hydrated oxides are precipitated by ammonia, subsequently dissolved in hydrochloric acid, and precipitated as oxalates. These last are converted into the sulphates, and from the mixed salts thorium sulphate is obtained by dissolving in ice-cold water, in which it is less soluble than the sulphates of the accompanying metals. This fractional crystallisation from ice-cold water is repeated several times. The sulphate crystallises with 8 mols. H_2O. From the anhydrous salt, the equivalent of the metal is determined by ignition and weighing the residual oxide; the mean value of eight concordant determinations is 57·997. The sp. gr. of the anhydrous sulphate is 4·2252.

Specimens of the chloride were obtained by heating the metal in a current of dry hydrochloric acid at a low red heat and subsequent resublimation of the salt. The percentage of chlorine found was 37·83 (theory requiring 37·89). Vapour-density determinations of different samples at temperatures varying from 1057° to 1270° gave values from 11·232 to 12·424; a determination at 1400° gave the value 9·835. The theoretical value for the chloride $ThCl_4$ is 12·928. The previous determinations of Troost, which varied from 5·9 to 7·49, were probably vitiated by impurities in the samples used.

Then as thorium is quadrivalent, no place being found for a bivalent metal of atomic weight 116 in the periodic system, as also from the values found for the sp. gr. of the anhydrous sulphate and oxide, the corrected atomic weight is taken as 231·813 to 231·916 (mean 231·87), oxygen being taken as 15·96. V. H. V.

Potassium Germanium Fluoride. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 1696—1700).—Germanium fluoride is readily obtained in solution by dissolving the oxide in hydrofluoric acid; on evaporating the solution with sulphuric acid and subsequent ignition the oxide is re-formed. On adding potassium hydrogen fluoride to the solution of germanium fluoride, the double salt is precipitated at first as a gelatinous precipitate, which gradually becomes crystalline;

on slowly evaporating the saturated solution, it separates in the form of tables or prisms. The salt can be heated to a red heat without alteration in weight. Its composition, K_2GeF_6, was determined by evaporating the salt with sulphuric acid and igniting, and weighing the residue of the oxide GeO_2 and potassium sulphate. It is shown by crystallographic measurements ($a : c = 1 : 0{\cdot}8039$) that this salt is isomorphous with ammonium silicofluoride. In conclusion, it is remarked that the properties of potassium germanium fluoride agree with those predicted by Mendelejeff for the corresponding salt of ekasilicon. V. H. V.

Alkaline Vanadates. By A. Ditte (*Compt. rend.*, **104**, 1168—1171).—When a mixture of lithium carbonate (1 mol.) and vanadic anhydride (1 mol.) is boiled with water, and the solution concentrated to a thick syrup in a vacuum, it deposits brilliant, silky needles of the composition $Li_2O,V_2O_5 + 4H_2O$, which lose water when heated, and form a brown liquid, which solidifies to a crystalline mass of the anhydrous normal vanadate.

If a solution of the normal vanadate is acidified with acetic acid and evaporated in a vacuum, it deposits red transparent crystals with a brilliant lustre, which have the composition $Li_2O,2V_2O_5 + 12H_2O$. If crystallisation takes place in a warm solution, thin orange-red plates of the composition $Li_2O,2V_2O_5 + 8H_2O$ are obtained.

When lithium carbonate is boiled with an excess of vanadic anhydride, and the solution slightly acidified with acetic acid, and concentrated in a vacuum, it deposits orange-red crystals of the compound $2Li_2O,3V_2O_5 + 16H_2O$.

All the hydrated acid salts when heated lose their water without melting and become deep red-brown. At a higher temperature, they melt to a brown liquid which solidifies to a crystalline mass on cooling.

If a solution of the normal vanadate is made strongly alkaline with lithia and concentrated in a vacuum, the syrupy liquid deposits silky, white needles of the compound $2Li_2O,V_2O_5 + 6H_2O$, which lose water when heated, then melt, and solidify on cooling to a white, crystalline, nacreous mass of the composition $2Li_2O,V_2O_5$. If the mother-liquor from these crystals is concentrated, it deposits crystals of the compound $3Li_2O,V_2O_5 + 6H_2O$.

Lithium carbonate solution saturated with vanadic anhydride, and mixed with a warm concentrated solution of lithia in large excess, almost immediately deposits the compound $4Li_2O,V_2O_5 + H_2O$ in transparent, microscopic crystals, which if left in contact with the mother-liquor change to bulky, colourless, transparent, rhomboidal crystals of the composition $4Li_2O,V_2O_5 + 14H_2O$. They lose water when heated, but the white, anhydrous salt is infusible even at a red heat.

A comparison of the various alkaline vanadates (Abstr., 1886, 671, and this vol., 639) shows that they are analogous in constitution, but contain different amounts of water of crystallisation according to the conditions under which they are formed. The normal salts are

colourless, the acid salts red with a more or less marked orange tint, and the basic salts are colourless. C. H. B.

Reduction of Potassium Niobium Fluoride with Sodium. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 1691—1696).—By heating potassium niobium fluoride with sodium, the mixture being protected by a layer of sodium chloride, Marignac obtained a black insoluble powder; this was found to consist of a hydride of niobium, NbH, mixed with a small quantity of niobic acid. In this paper, the experiments of Marignac are repeated; the product obtained on heating the mixture of potassium niobium fluoride, sodium, and sodium chloride, was treated at first with alcohol, then with water, and finally washed with ether. The product was a glistening, hygroscopic, black powder, unattacked by hydrochloric and nitric acids or aqua regia, but soluble in concentrated hydrofluoric acid with evolution of hydrogen. It burns in a current of dry hydrochloric acid gas with formation of four different chlorides of niobium, two of which are the more and two the less volatile in the gas. Analysis showed the composition of the product to be as follows: —NbH = 77·5 per cent.; Nb_2O_5 = 21·53 per cent.; Fe_2O_3 = 0·97 per cent.

The following determinations are also given of the molecular heats of niobium hydride and oxide:—

	Molecular heats at			
	100—0°.	210·5—0°.	301·5—0°.	449—0°.
Niobium hydride....	9·3	8·8	8·3	7·9
Niobic acid	31·7	31·8	33·3	36·1

V. H. V.

Earths and Niobic Acid from Fergusonite. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 1676—1690.)—In this paper, a description is given of the qualitative separation of the various earths present in the mineral fergusonite, a large quantity of which was operated on. The two samples used came from Arendal and Ytterby.

Among the oxides of the rare metals found were those of cerium, thorium, erbium, samarium, thulium, ytterbium, and the various components of didymium, and of Soret's X. Among the acid-forming oxides were those of titanium, tantalum, and niobium.

In order to prepare pure niobic acid from the mineral, the aqueous solution of crude potassium niobium oxyfluoride is heated for some time to separate the oxyfluoride of potassium and tantalum, $2(2KF,TaF_5),Ta_2O_5$; on subsequent evaporation, the niobium oxyfluoride, $2KF,NbOF_3$, crystallises out, and from the determination of the ratio $2K_2SO_4 : Nb_2O_5$ obtained from the salt, the atomic weight of niobium is taken as 93·8. From the oxyfluoride, a sample of the double fluoride K_2NbF_7 was obtained, and from the ratio $2K_2SO_4 : Nb_2O_5$ the value 93·96 is deduced; these numbers are practically equal to the atomic weight 94 taken by Marignac. When a solution of potassium niobium oxyfluoride is boiled, a double salt, $2KF,3NbO_2F$,

separates as a hard white powder consisting of minute crystals. The change which leads to its formation may be expressed thus:

$$3(2KF,NbOF_3,H_2O) = 2KF,3NbO_2F + 4KHF_2 + 2HF.$$

V. H. V.

Mineralogical Chemistry.

Bismuthic Gold. By R. W. E. MacIvor (*Chem. News*, **55**, 191).—An analysis of bismuthic gold from Maldon, Victoria, gave gold 64·211; bismuth 34·398; siliceous matter 1·391 per cent. The proportions of gold and bismuth indicate the formula Au_2Bi.

R. R.

Enargite from Montana. By W. Semmons (*Min. Mag.*, **6**, 49—51; *Jahrb. f. Min.*, 1887, **1**, Ref., 416—417).—The mineral examined was of a lead-grey colour, with a black streak; sp. gr. 4·3, hardness 2·5. Crystals are rare and always small. The crystals are rhombic prisms with brachypinacoid and macropinacoid, brachydomes and macrodomes. Analysis gave the following results:—

	Cu.	As.	S.	SiO_2.	Fe.	Total.
I....	45·76	18·66	31·30	2·50	0·80	99·02
II....	47·84	19·47	32·69	—	—	100·00

Analysis II gives the results calculated to 100, the silica and iron being considered as impurities. The mineral thus very closely resembles enargite in composition, but differs from it in cleavage, in hardness, and in behaviour before the blowpipe. It occurs with iron pyrites, bornite, covelline, and quartz in a number of mines in Montana, United States.

B. H. B.

Artificial Production of Rose Spinel or Balas Ruby. By S. Meunier (*Compt. rend.*, **104**, 1111—1112).—The bottom of a graphite crucible is covered with a layer of finely-powdered magnesia well rammed down, an intimate mixture of very finely-powdered aluminium chloride and cryolite is then introduced, and the crucible is filled up with alumina and magnesia, the latter being in excess. If a rose-coloured product is desired, a very small quantity of potassium dichromate is added. The crucible is heated for five or six hours in a good coke fire, and allowed to cool as slowly as possible. The product is a greyish gangue, full of vesicles which are lined with brilliant, rose-coloured crystals of balas ruby, identical with the natural crystals in form, colour, brilliancy, hardness, and optical properties. If cryolite is used without aluminium chloride, the product consists of rose-coloured lamellæ of corundum without any trace of spinel, even in presence of a large excess of magnesia.

Probably this is a further example of the mineralising action of fluorine recently described by Fremy (this vol., p. 556). The experiment may be varied in many ways, and the author has obtained a

series of products which includes the aluminates of zinc, iron, &c., together with secondary products. C. H. B.

Artificial Production of Magnetite. By A. Gorgeu (*Compt. rend.*, **104**, 1174—1177).—When a mixture of ferric and ferrous sulphates is decomposed in a bath of fused sodium sulphate, crystals of ferric oxide only are formed, and no magnetite is obtained. The latter is only produced if some reducing agent is introduced at the moment when the whole of the iron has been oxidised to the ferric state. Ferric oxide answers quite as well as the mixed sulphates.

When iron wire or turnings is introduced into fused sodium sulphate, a small quantity of sulphurous anhydride is evolved, and some free soda is formed, but the main product is a magnetic ferrous ferrite, containing a much larger proportion of ferrous oxide than magnetite. If the action of heat is continued, the ferrite undergoes oxidation, the sulphite and sulphide are reoxidised to sulphate, and eventually the whole of the iron is converted into the crystalline magnetic oxide. If the substances taken are weighed, it is found that the increase of weight at the close of the experiment is sensibly equal to the oxygen absorbed by the iron, the sodium sulphate having absorbed from the air a quantity of oxygen equal to that which it gave up to the iron. Potassium sulphate gives similar results.

Iron sulphides act energetically on fused alkaline sulphates, with evolution of a large quantity of sulphurous anhydride, and ultimate formation of magnetite and an alkaline sulphate. The alteration in weight is due to the loss of the sulphur originally present in the sulphide, and the absorption of 1·33 times its weight of oxygen by the iron in the sulphide. The yield is better the greater the intermediate formation of a double alkaline ferrous sulphide, and is best of all when a mixture of sodium sulphide and sulphite is used instead of the sulphate.

Artificial magnetite very closely resembles the natural mineral. It crystallises in opaque, magnetic octahedra with a metallic lustre, which are sometimes modified by very small faces of the rhombic dodecahedron; hardness 6·0—6·5; sp. gr. 5·21—5·25. The hardness and sp. gr. of the natural mineral are 5·5—6·5 and 4·9—5·27 respectively. The artificial crystals are not affected by water and carbonic anhydride at a bright red heat, are not attacked by nitric or hydrochloric acid diluted with 10 vols. of water, and are only very slowly dissolved by the strong acids or aqua regia. When roasted in the air, they yield pure ferric oxide, and the residue is usually not magnetic, but if the magnetite has been prepared from native ferrous carbonate the residue is magnetic, a result which is doubtless due to the presence of foreign ferrites. C. H. B.

Australian Bat Guano and Minerals occurring therein. By R. W. E. MacIvor (*Chem. News*, **55**, 215—216).—The author gives the results of his examination of bat guano obtained from caves situated in various parts of Victoria. The only important deposit is at the Skipton caves, about 30 miles from Ballarat. Disseminated

through these deposits are crystals of Struvite (I), and of Hannayite (II), and Newberyite (III), minerals previously described by the author, of which the following new analyses are given :—

	MgO.	FeO.	MnO.	$(NH_4)_2O$.	P_2O_5.	Water.
I....	16·07	0·81	0·16	10·57	28·82	(43·57)
II....	18·54	0·31	0·09	8·10	44·71	(28·25)
III....	22·37	0·85	0·21	—	40·73	(35·84)

Reference is made to two new ammonio-magnesium phosphates, Muellerite and Dittmarite, which will be described later.

A. J. G.

Destinezite. By G. Cesáro (*Jahrb. f. Min.*, 1887, **1**, Ref., 412—413).—The author has made a chemical and crystallographical investigation of an almost white destinezite from Visé. On heating from 130° to 250°, 1 gram of the mineral lost 0·09 to 0·242 gram of volatile matter. At a red heat it lost 0·445 gram. Analysis gave the following results :—

Insoluble residue.	Fe_2O_3.	P_2O_5.	SO_3.	H_2O.	Hygroscopic H_2O.	Total.
1·40	37·60	16·76	18·85	25·35	0·30	100·26

From these results, the author calculates the formula $P_2O_5,Fe_2O_3 + Fe_2O_3,2SO_3 + 12H_2O$. He concludes that the constitution of the substance is $O[Fe_2(OH)(SO_4H) : PO_4]_2 + 10H_2O$. Under the microscope, it is seen that destinezite forms small crystals at least 0·01 mm. in length. They are colourless, and isomorphous with gypsum.

B. H. B.

Wollastonite from Sardinia. By L. Busatti (*Jahrb. f. Min.*, 1887, **1**, Ref., 420).—The mineral examined was found at S. Vito, in the mining district of Sarrabus in Sardinia. It forms rosette-shaped aggregates of greyish-white fibres on a black Silurian clay slate. The substance is fusible with difficulty before the blowpipe, and gelatinises when heated with concentrated hydrochloric acid. Its hardness is $4\frac{1}{2}$, and its sp. gr. 2·7 to 2·8. From the analysis, the formula $CaSiO_3$ was deduced. The analytical results were as follows :—

SiO_2.	CaO.	MgO.	Fe_2O_3.	H_2O.	Total.
49·78	45·12	1·20	2·20	0·60	98·90

B. H. B

Griqualandite. By G. Hepburn (*Chem. News*, **55**, 240).—This mineral, from Griqualand West, South Africa, appears to be a pseudomorph after crocidolite, which it exactly resembles in structure. It has, however, the composition of a ferric silicate, $6SiO_2,4Fe_2O_3,5H_2O$. It occurs as opaque, asbestos-like fibres, non-elastic, and of a snuff or golden-brown colour. The analytical results were—

SiO_2.	Fe_2O_3.	H_2O combined.	FeO.	MgO.	Moisture.	Total.
56·75	37·64	4·96	1·09	0·10	0·27	100·81

R. R.

The Meteorite of Karang-Modjo or Magetan in Java. By J. Bosscha (*Jahrb. f. Min., Beilage* **5**, 126—144).—The Leyden Museum possesses a fine meteorite, described in the catalogue as the Magetan meteorite. It fell on October 3, 1883, at Karang-Modjo, in the Magetan district of Java. On the same day, the Ngawi meteorite fell in the same settlement. It is consequently highly probable that both meteorites belong to the same fall. The Magetan meteorite weighed 1191·1 grams. Its sp. gr. was found to be 3·34. In macroscopic and microscopic structure the Magetan and Ngawi meteorites are identical. B. H. B.

Sulphuretted Waters of Olette (Pyrénées Orientales). By E. Willm (*Compt. rend.*, **104**, 1178—1180).—These springs are the hottest and most copious in the Pyrenees. There are also two which may be regarded as degenerated sulphuretted waters, since their general composition is the same, but they contain a larger proportion of sulphates, and no sulphides or thiosulphates. They also contain a notable quantity of nitrates.

	Sulphuretted.				Degenerated.	
Name of spring	Cascade.	St. André.	Eau-Bonne.	No. 4.	Cérola.	No. 23.
Temperature	79·4°	74·9°	42·2°	41·5°	52·5°	33·1°
Sulphur as sulphides....	0·0078	0·0096	0·0064	0·0057	—	—
Thiosulphuric acid (S_2O_3)	0·0111	0·0113	0·0110	0·0098	—	—
Sulphuric acid (SO_4) ...	0·0168	0·0184	0·0210	0·0300	0·0416	0·0411
Chlorine	0·0101	0·0110	0·0107	0·0105	0·0102	0·0136
Nitric acid (NO_3)	—	—	—	—	0·0260	0·0174
Silica	0·0898	0·0866	0·0876	0·0860	0·0880	0·0895
Sodium	0·0602	0·0606	0·0592	0·0592	0·0606	0·0590
Potassium	0·0046	0·0062	0·0051	0·0051	0·0037	0·0040
Calcium	0·0024	0·0020	0·0020	0·0024	0·0040	0·0092
Magnesium	traces	0·0001	traces	traces	0·0002	0·0003
Total carbonic anhydride	0·0410	0·0448	0·0444	0·0480	0·0520	0·0759

All the waters contain traces of phosphoric and boric acids, iodine, and arsenic, but are free from ammonia. The nitrates were estimated by converting them into ammonia by means of the zinc-copper couple.

The nitric acid is probably due to the nitrification of air which has come in contact with the water at a great depth, the change being assisted by the high temperature and pressure. The increase in the proportion of the calcium carbonate may be attributed to the action of the carbonic anhydride of this air on the surrounding rocks. The similarity between the composition of the sulphuretted waters and of the degenerated waters shows that there has not been any infiltration of surface water. C. H. B.

Organic Chemistry.

Determination of the Relative Values of the Four Units of Chemical Activity of the Atom of Carbon. By L. Henry (*Compt. rend.*, **102**, 1106—1109).—Hitherto there has been no actual determination of the relative values of the four units of chemical activity of the atom of carbon. Monocarbon-compounds of the type CX_4 will of course exist only in one form whatever the relative values of the four units, but if these values are different, monocarbon-compounds which contain two radicles should show differences. To take the simplest case, if one combining unit differs in value from the three others, compounds of the type CX_3X' would exist in two forms, those of the type $CX_2X'X''$ in three forms, and those of the type $CXX'X''X'''$ in four. At present at least, the author's attention is confined to compounds of the type CX_3X'. The best known and most easily obtained of these are the mono-substitution-derivatives of methane. It is true that only one variety of each of these derivatives is at present known, but this fact is without value, since it is impossible to affirm that in different specimens formed under different conditions the radicles saturate different combining units.

It is essential to prepare the mono-substitution-derivatives MeX by a systematic series of reactions, such that it can be affirmed that the radicle X is united successively with each of the four units of activity of the carbon-atom. In other words, it is necessary to ascertain if the order of introduction of the radicle into the molecule of methane exerts any influence on the properties of the resulting compound. The compounds selected for this purpose are the nitromethanes and the acetonitriles, which are well known and can be prepared by means of reactions that do not involve the use of high temperatures. The author uses the letters α, β, γ, δ to denote the compounds in which the first, second, third, and fourth atoms of hydrogen respectively are replaced by the radicle NO_2 or CN.

The α-derivatives are obtained by the action of methyl iodide on potassium cyanide and silver nitrite respectively.

The β-nitro-derivative is prepared by the action of potassium nitrite on a salt of β-chloracetic acid, which is obtained by the action of chlorine on acetic acid formed from α-acetonitrile. The β-acetronitrile is prepared by the dry distillation of β-cyanacetic acid which is obtained by the action of potassium cyanide on β-chloracetic acid.

The γ-derivative is prepared by similar reactions from γ-chloracetic acid. This compound is formed by the dry distillation of γ-chloromalonic acid, which is obtained in the form of an ethyl salt by the action of chlorine on diethyl malonate, the malonic acid having been obtained from cyanacetic acid, $CN_\beta{\cdot}CH_2{\cdot}COOH_\alpha$.

The δ-derivatives are formed in a similar manner from δ-monochloracetic acid, which is obtained by the action of heat on δ-chloromethine-carboxylic acid, $CCl(COOH)_{3\alpha\beta\gamma}$, and this is prepared by the action of ethyl chlorocarbonate on ethyl monosodiomalonate.

The α-, β-, and γ-derivatives have already been prepared by these methods and their properties investigated, but no differences could be detected. The δ-derivatives are being prepared.

The whole argument is of course based on the principle of substitution and the stability of complex molecular structures throughout the course of a chemical reaction. C. H. B.

Action of Bromine on Isobutylene. By L. M. Norton and H. J. Williams (*Amer. Chem. J.*, **9**, 87—89).—During the preparation of isobutylene bromide from pure isobutylene, it was noticed that a considerable quantity of a tribromisobutane was formed, boiling at 173—183° at a pressure of 235 mm. When treated with alcoholic soda, it yielded a liquid boiling at 158—161°; probably an isobutylene bromhydrin.

For purposes of comparison, a known tribromisobutane was prepared, namely, isobutylene bromide was converted by soda into isocrotyl bromide (b. p. 91—92°), and this saturated with bromine; the tribromide thus obtained boiled however at 155—161° at a pressure of 235 mm., and when treated with soda yielded a dibromisobutylene boiling constantly at 154—155°, and by addition of bromine it yielded a crystalline tetrabromisobutane, melting at 205°.

The two tribromisobutylenes are therefore not identical; that derived from isocrotyl bromide is $CMe_2Br \cdot CHBr_2$, and the only possible formula for that from isobutylene is $CMeBr(CH_2Br)_2$. This tribromide is not formed by the direct action of bromine on isobutylene bromide. H. B.

Synthetic Acetonitrile. By L. Henry (*Compt. rend.*, **104**, 1181—1184).—Acetonitrile is obtained only in very small quantity by the action of methyl hydrogen sulphate on potassium cyanide. Much better results are obtained by the action of methyl iodide on potassium cyanide. Schlagdenhauffen has stated (*Compt. rend.*, **48**, 228) that these compounds will not react under ordinary pressure but only in sealed tubes at about 100°. This statement is not strictly correct. Methyl iodide, alone or dissolved in acetonitrile, has no action on potassium cyanide even at its boiling point, but if it be mixed with aqueous methyl or ethyl alcohol the reaction begins after a short time at the ordinary temperature, becomes more rapid, with continual development of heat, and the liquid soon enters into energetic ebullition. Only a very minute quantity of hydrocyanic acid, if any, is evolved, and the liquid remains colourless. The reaction is complete, and the yield is almost quantitative. The facility with which potassium cyanide is attacked by methyl iodide contrasts with the difficulty with which it is decomposed by ethyl iodide, and the simplicity of the chemical change is in contrast with the complexity of the corresponding reaction with the iodo-derivatives of the higher homologues.

The methyl iodide and potassium cyanide are mixed in equivalent proportions, and methyl alcohol of 85 per cent. is added in quantity equal to about one-third the volume of the methyl iodide. After the first product is distilled off, the distillate is mixed with a fresh quantity of potassium cyanide and methyl iodide, and the process is repeated until sufficient acetonitrile has been obtained. The product is treated with calcium chloride to remove the water and methyl alcohol, redistilled, and finally dried over phosphorus pentoxide. The pure product obtained is about 81 per cent. of the theoretical.

The acetonitrile prepared in this way is identical with that obtained by the dehydration of acetamide. C. H. B.

Dichlorethyl Alcohol. By M. de Lacre (*Compt. rend.*, **104**, 1184—1186).—This compound is obtained by means of a reaction similar to that which serves for the preparation of trichlorethyl alcohol. Zinc ethyl (1 mol.) dissolved in purified ether is placed in a flask filled with carbonic anhydride and surrounded by cold water, and dichloraldehyde (2 mols.) dissolved in ether is added very gradually. A violent reaction takes place, and a semi-solid substance of the composition $(CHCl_2\cdot CH_2\cdot O)_2Zn$ separates. When this is decomposed by treatment with water and the liquid distilled, the products separated by fractionation are hydrated dichloraldehyde, dichlorethyl alcohol, and a crystalline solid which volatilises at a moderate temperature, the quantities obtained amounting respectively to 28, 38, and 15 per cent. of the dichloraldehyde used.

Dichlorethyl alcohol, $CHCl_2\cdot CH_2\cdot OH$, is a colourless thick viscous liquid with a characteristic odour and a pungent taste. It does not solidify in a mixture of sodium sulphate and hydrochloric acid, but boils without decomposition at 146° under a pressure of 764 mm.; sp. gr. at 15° = 1·145; vapour-density 3·93. It is only slightly soluble in water, but dissolves readily in alcohol and ether, reduces ammonio-silver nitrate, and does not dissolve and is not affected by calcium chloride. It is attacked with some difficulty by fuming nitric acid, the product being dichloracetic acid, which boils at 191°.

When treated with phosphorus pentachloride, dichlorethyl alcohol yields monochlorethylene chloride, $CHCl_2\cdot CHCl$, boiling at 114—115°. With phosphorus tribromide, it yields the corresponding bromine-derivative which boils at 138°, and is identical with the compound prepared by Henry (Abstr., 1884, 571) by the action of antimony pentachloride on monobrom- or monochlor-ethylene bromide.

Dichlorethyl nitrate, $CHCl_2\cdot CH_2\cdot NO_3$, is obtained by the action of nitrosulphuric acid on the alcohol. It is a colourless liquid with a penetrating, ethereal odour and a sweet, aromatic taste. It is insoluble in water and boils at 155—156° under a pressure of 767 mm.; vapour-density 5·56.

Dichlorethyl acetate, $CHCl_2\cdot CH_2\cdot OAc$, is obtained by the action of acetic chloride on the dichloralcohol. It is a colourless liquid with a strong pleasant odour, different from that of its isomeride ethyl dichloracetate, and a very piquant taste. It boils at 166—168° under a pressure of 766 mm.; vapour-density 5·74; sp. gr. at 15° = 1·104.

C. H. B.

Normal Butyl Alcohol in Cognac Brandy: Higher Alcohols in Brandy and the Products of Fermentation of Sugar by Elliptical Yeast. By E. Claudon and E. C. Morin (*Compt. rend.*, **104**, 1187—1189).—250 grams of the oils obtained by Ordonneau from brandy (Abstr., 1886, 436) were dried over potassium carbonate, distilled from barium oxide, and fractionated. The percentage composition of the fraction containing the higher alcohols was as follows:—

	Claudon & Morin.	Ordonneau.
Propyl alcohol	11·9	11·7
Isobutyl alcohol	4·5	0·0
Normal butyl alcohol	49·3	63·8
Amyl alcohol	34·4	24·5

Ordonneau's figures are given for comparison. The normal butyl alcohol was recognised by its vapour-density and by converting it into the corresponding iodide. These results confirm those obtained by Ordonneau. The presence of butyl alcohol and butyric acid in this brandy may in all probability be attributed to the development of a bacillus in the wine from which the brandy was made. *Bacillus butylicus*, which converts glycerol, sugar, &c., mainly into normal butyl alcohol and butyric acid, will produce energetic fermentation even in a liquid containing as much as 10 per cent. of ethyl alcohol.

The following table shows the relative proportions of the higher alcohols in cognac brandy and in the corresponding product obtained from sugar fermented by elliptical yeast. The figures give the amounts of the higher alcohols in each hectolitre of the alcohol taken at 100°. The normal butyl alcohol present in the cognac is omitted.

	Cognac.	Sugar, with elliptical yeast.
Propyl alcohol	48·1	3·1
Isobutyl alcohol	18·5	2·4
Amyl alcohol	139·5	80·0
	206·1	85·5

It is evident that elliptical yeast alone gives a much lower proportion of the higher alcohols than is contained in wine fermented in the ordinary manner, and hence the practice of "sugaring," at least from this point of view, cannot be injurious. C. H. B.

Action of Sodium Amalgam on Arabinose. By H. Kiliani (*Ber.*, **20**, 1233—1235).—When arabinose is treated with sodium amalgam, with gradual addition of dilute sulphuric acid to prevent the reaction from becoming alkaline, and the product extracted with alcohol, a crystalline substance is obtained, which does not reduce Fehling's solution and has no specific rotatory power. This compound is probably a pentatomic alcohol, $OH{\cdot}CH_2[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH$; it is thus proposed to call it *arabitol*. It melts at 102°, and in this

property resembles sorbite, from which it differs in that it loses water neither at 100° nor when left in a vacuum. V. H. V.

Sugar from Hesperidin and Naringin. By W. Will (*Ber.*, **20**, 1186—1190).—When hesperidin is decomposed by dilute sulphuric acid and the sugar so obtained dissolved in alcohol and fractionally precipitated, well-formed crystals of isodulcitol were obtained. Glucose is also present. The two are readily separated by means of their phenylhydrazine-compounds. *Isodulcitolphenylhydrazine* crystallises in yellow needles melting at 180°; it is insoluble in water, soluble in warm alcohol and glacial acetic acid; it is separated from the phenylglucazone by extracting with boiling acetone, in which it is soluble.

Crude maringin sugar, when treated with phenylhydrazine hydrochloride and sodium acetate, also yields the phenylhydrazine-derivatives of isodulcitol and grape-sugar, and is therefore identical with the sugar from hesperidin. N. H. M.

Sodium Nitrate in Gun-cotton. By F. Nettlefold (*Chem. News*, **55**, 241).—This paper gives weighings showing the hygroscopic effect of sodium nitrate in gun-cotton charges. R. R.

Hydrazine (Diamidogen). By T. Curtius (*Ber.*, **20**, 1632—1634).—Ethyl diazoacetate, when treated with hot concentrated aqueous potash, is converted into the potassium salt of a new diazo-fatty acid, which crystallises in large yellow prisms, and differs from all diazo-fatty compounds hitherto described, since the addition of mineral acids does not bring about the evolution of nitrogen, but results in the separation of the diazo-acid in the form of glistening, golden-yellow tablets. These dissolve in water with a golden-yellow colour, and when the solution is digested for a short time with very dilute sulphuric acid, the colour disappears without evolution of nitrogen, and on cooling the sulphate of a new inorganic base, *hydrazine*, $NH_2{\cdot}NH_2$, is obtained in colourless, well-defined crystals.

Hydrazine sulphate, N_2H_4,H_2SO_4, crystallises in anhydrous tables showing a vitreous lustre, and is sparingly soluble in cold, readily soluble in hot water, insoluble in alcohol. It is not decomposed at a temperature of 250°, but when heated over a flame, it melts with an explosive evolution of gas, accompanied with a partial reduction of the sulphuric acid to sulphur. The *hydrochloride*, $N_2H_4,2HCl$, obtained from the sulphate by treating it with barium chloride, forms large regular crystals, melts at about 200° with evolution of gas, and is readily soluble in cold water, less soluble in alcohol. With platinic chloride, it does not form a double salt, but is decomposed with the evolution of much gas.

Diamidogen or *hydrazine*, $NH_2{\cdot}NH_2$, is obtained when its salts are heated with aqueous soda. It is a very stable gas, is extremely soluble in water, turns red litmus-paper a deep blue, and gives white fumes with acid vapours. In the concentrated state, it has a very peculiar odour only slightly resembling that of ammonia, and, when breathed, it powerfully affects the nose and throat. When the

hydrochloride is heated with dilute aqueous soda, and the water which passes off by evaporation is constantly renewed, small quantities of hydrazine pass over with the steam even at the end of half an hour; and if, instead, the solution is allowed to concentrate, and finally is heated to the fusing point of sodium hydroxide, no formation of ammonia occurs, but the greater part of the base distils over with the steam. Hydrazine is a very powerful reducing agent, and in its reactions exhibits all the properties of its substitution derivatives. Fehling's solution and ammoniacal silver solution are at once reduced by it in the cold; from neutral copper sulphate a thick, red precipitate, from mercuric chloride a white precipitate, and from aluminium salts alumina are obtained, whilst with aromatic aldehydes and ketones it yields sparingly soluble, crystalline compounds. The solutions of the salts of hydrazine are decomposed by nitrites with much frothing. W. P. W.

Oxidation of Ricinoleic and Linoleic Acids. By W. Dieff and A. Reformatsky (*Ber.*, **20**, 1211—1212).—By oxidising ricinoleic and linoleic acids by means of potassium permanganate in alkaline solutions, trihydroxy- and tetrahydroxy-stearic acids respectively were obtained. The linoleic acid must therefore contain 18 and not 16 carbon-atoms. N. H. M.

New Reactions with Ethyl Sodacetoacetate and Ethyl Sodomalonate. By A. Michael (*Amer. Chem. J.*, **9**, 124—129).—Ethyl sodacetoacetate and benzaldehyde react to form a crystalline substance melting at 126—127°, and quite different from the compound described by Claissen. Ketones do not react until heated to 100°. Ethereal thiocarbimides react readily. Thus phenyl thiocarbimide and ethyl sodomalonate yield a crystalline substance, $C_{14}H_{15}NaSNO_4$, from which acids separate the thioanilide,

$$NHPh\cdot SC\cdot CH(COOEt)_2,$$

melting at 60°. Phenyl isocyanate reacts at once with ethyl sodacetoacetate, yielding two products, whilst with ethyl sodomalonate three products are obtained, the only one described being the sodanilide of methenyldiethyltricarboxylate, $NNaPh\cdot CO\cdot CH(COOEt)_2$, melting at 123—124°; from this, by treatment with acids, a compound, $C_{12}H_9NO_3$, melting at 172°, is obtained. Phthalic anhydride reacts readily, yielding a heavy oil of acid properties, having the formula $C_{14}H_{14}O_6$. Carbonic anhydride, carbon bisulphide, sulphurous anhydride, and phosphoric anhydride react readily with ethyl sodomalonate forming new compounds. The formation of coumarins by dehydrating a mixture of ethyl acetacetate and resorcinol has already been described; using ethyl sodacetoacetate, condensation takes place in the cold, and β-methylumbelliferone may be thus easily prepared. Sulphur seems to form ethyl thiotartronate with ethyl sodomalonate. The carbamides react to form ureides: thus sodium barbiturate is formed from urea and ethyl sodomalonate, and similarly a thiobarbiturate is obtained from thiocarbamide. Acetamide yields with ethyl sodomalonate a substance of the formula $C_7N_2Na_2H_8O_4$, and aldehyde ammonia and

ethyl sodacetoacetate yield long white needles of a compound of the formula $C_8H_{12}NNaO_2$.

H. B.

Ethyl Propiopropionate. By A. Hantzsch and O. Wohlbrück (*Ber.*, **20**, 1320—1325).—Ethyl propiopropionate, recently investigated by Israel (Abstr., 1886, 334), is probably the ethyl salt of an α-acid, and not of a β-acid, in that, like ethyl acetoacetate, it is decomposed by hydrolysis into a ketone and carbonic anhydride, the acid which is formed as an intermediate product being exceedingly unstable. When reduced with sodium amalgam, it is converted into a lactic acid, *α-methyl-β-hydroxyvaleric acid*, $CH_2Me{\cdot}CH(OH){\cdot}CHMe{\cdot}COOH$, an uncrystallisable syrup, the sodium salt of which crystallises in leaflets. By phosphoric iodide, it is converted into methylpropylacetic acid, $CH_2Me{\cdot}CH_2{\cdot}CHMe{\cdot}COOH$, which boils at 191—194°, and differs from primary caproic acid, in that it gives a flesh-coloured precipitate with ferric chloride. The monobromo-substitution derivative of ethyl propiopropionate is converted at 100° into a crystalline mass of an acid homologous with tetric acid, probably *α-propioacrylic acid*, $COEt{\cdot}CH:CH{\cdot}COOH$, which crystallises in colourless tablets, melting at 106—108°. With nitrous acid, ethylic propiopropionate yields *ethyl α-oximepropionate*, $NOH:CMe{\cdot}COOEt$, melting at 94°. Levulinic acid, under similar conditions, yields a substance of the composition $C_{10}H_{14}N_4O_{11}$, which may empirically be regarded as compounded of 2 mols. of di-isonitrosolevulinic acid with 1 mol. of water.

V. H. V.

Synthesis of Diatomic Monobasic Acids from Ketones. By S. Reformatsky (*Ber.*, **20**, 1210—1211).—β-Dimethylethylenelactic acid (hydroxyvaleric acid) is obtained by the action of ethyl monochloracetate and zinc on acetone. The author proposes to investigate the reaction between ethyl sodacetate and zinc, and other ketones as well as aldehydes and the alkyl salts of monobasic acids.

N. H. M.

Decomposition of Ethyl Acetomalonate and its Homologues. By E. Lang (*Ber.*, **20**, 1325—1328).—With a view of preparing higher homologues of ethyl acetoacetate, the decomposition of ethereal salts of substituted malonic acids by nitrous acid was investigated. It is found that by this reaction isonitroso-derivatives of ethyl acetoacetate are produced.

Ethyl propiomalonate, $COOEt{\cdot}CH(COEt){\cdot}COOEt$, is a colourless liquid boiling at 239—242°; *ethyl butyromalonate* boils with partial decomposition at 247—252°, and the *ethyl isonitrosobutyroacetate*, derived from it, is a yellow oil, soluble in alkalis with red coloration.

V. H. V.

Glycuronic Acid. By H. Thierfelder (*Zeit. physiol. Chem.*, **11**, 388—409).—This substance, which was first obtained from the urine of dogs by Schmiedeberg and Meyer (*Zeit. physiol. Chem.*, **3**, 422), was shown to exist in purree by Spiegel (Abstr., 1883, 219, and this

vol., p. 498). It may be prepared in a pure state as follows:—Purree is mixed with water, and digested with hydrochloric acid, the excess of which is removed by filtering, and washing the precipitate with water; the euxanthic acid which is insoluble in water is dissolved in hot alcohol, and on cooling separates in yellow needles; it is purified by repeated recrystallisation. Spiegel's method of decomposing this acid into euxanthone and glycuronic acid by weak sulphuric acid not giving good results, it was found better to mix it with water and subject it to a temperature of 120—125° in a Papin's digester for some hours. On cooling, yellow needles of euxanthone form, and are filtered off. The filtrate is twice more subjected to the same process. The acid filtrate is then concentrated to a thin syrup by means of an air-pump. Large brown crystals of glycuronic anhydride separate; they are obtained colourless by recrystallisation. Free glycuronic acid is easily obtained by the action of sulphuric acid on the barium salt. The anhydride may also be obtained from this by heating its aqueous solution; the crystals belong to the monoclinic system, and have a sweetish, somewhat bitter, taste. The lead and barium salts were described by Schmiedeberg and Meyer. The potassium salt crystallises in colourless, strongly refracting needles with four prismatic faces, having the composition $C_6H_9O_7K$. The sodium salt is as easily obtained, and crystallises in fine needles arranged in a dendritic or radial manner. Attempts to crystallise the zinc, cadmium, copper, calcium, and silver salts failed. By mixing solutions of glycuronic anhydride with phenylhydrazine hydrochloride and sodium acetate, according to Fischer's method (Abstr., 1885, 53), brown drops form and sink to the bottom of the vessel, where they form a sticky, black mass; this is a compound of glycuronic acid with phenylhydrazine, but a similar product in a form available for analysis may be obtained by using a solution of potassium glycuronate instead of the anhydride. Yellow needles are then formed, of neutral reaction, melting point 114—115°, and composition $C_{42}H_{48}N_{10}O_{10}$. They reduce Fehling's solution on the application of heat. Attempts to obtain a benzoyl compound by Baumann's method (this vol., p. 228) failed.

The specific rotation of the anhydride is $[\alpha]_D = +19{\cdot}25$; Külz gives 19·4 (this vol., p. 498). Difference of temperature, however, probably accounts for the discrepancy, the present determinations being made at 18°, those of Külz at 21°. Experiments moreover showed that the specific rotation rises with the temperature of the solution.

Glycuronic acid reduces copper and bismuth salts in warm alkaline solutions; comparing its reducing power with that of dextrose, 1 part of the latter corresponds with 0·989 of glycuronic anhydride.

By the action of bromine, it yields saccharic acid. By the action of sodium amalgam, gluconic acid is obtained. By the action of mineral acids, lævulinic acid is not obtained but an acid containing two atoms of hydrogen less ($C_5H_6O_3$). W. D. H.

Thiënethylamine. By H. Goldschmidt and W. Schultheiss (*Ber.*, **20**, 1700—1701).—As the method of preparation of amines from the

oximes has been shown to be applicable to the furfuran-derivatives, it is here applied to thiophen-compounds. Thus, acetothiënoxime is converted on hydrogenation into *thiënethylamine*, $C_4SH_3 \cdot CHMe \cdot NH_2$. This reaction is best effected in a freezing mixture. The resultant compound is a colourless liquid, boiling at 185—187°; it absorbs carbonic anhydride from the air, is decomposed on evaporation with hydrochloric acid; with acetic acid, it yields an acetate, $C_6H_9SN \cdot OAc$, crystallising in colourless, very soluble needles. Its benzoyl-derivative forms glistening, white needles melting at 95°, and gives the indophenine reaction. V. H. V.

Constitution of Benzene. By A. Claus (*Ber.*, **20**, 1422—1426).—The author considers that the introduction of three pairs of quinone-oxygen atoms in benzene (Nietzki and Kehrmann, this vol., p. 473), can only be simply explained by his diagonal formula for benzene, and discusses the point raised against the diagonal formula, that it does not show a difference between ortho- and para-positions. The benzene formula lately suggested by J. Thomsen (*Ber.*, **19**, 2944) is criticised, and R. Meyer's octahedral formula (*Ber.*, **15**, 1825) referred to. N. H. M.

Aromatic Nitriles: Action of Sodium and Alcohol on α-Naphthonitrile, Benzonitrile, and Tolunitrile. By E. Bamberger and W. Lodter (*Ber.*, **20**, 1702, and 1703—1710).—On hydrogenation of the aromatic nitriles two classes of substances are formed, namely, the corresponding hydrocarbon, or more generally its dihydro-derivative, thus: $C_{10}H_7 \cdot CN + 2H_2 = C_{10}H_{10} + HCN$, and the primary amine; and in part its tetrahydro-derivative, thus: $C_{10}H_7 \cdot CN + 4H_2 = C_{10}H_{11} \cdot CH_2 \cdot NH_2$.

Dihydronaphthalene, $C_{10}H_{10}$, formed as in the above reaction, is a strongly refractive oil, boiling at 211° under 713 mm. pressure, and solidifying at low temperatures in large, glistening tables which melt at 15·5°. It readily takes up bromine to form a dibromide, $C_{10}H_{10}Br_2$, which crystallises in colourless prisms of the monoclinic system, melting at 73·5—74°, and is readily converted into naphthalene with evolution of hydrobromic acid.

Tetrahydronaphthobenzylamine, $C_{10}H_{11} \cdot CH_2 \cdot NH_2$, also obtained in the above reaction, is a colourless, strongly refractive, viscid oil, of peculiar ammoniacal odour, boiling at 269—270° under 722 mm. pressure. It is monobasic, and shows a remarkable affinity for carbonic anhydride. Its *hydrochloride* crystallises in needles; its *platinochloride* is a pale-yellow, crystalline precipitate. On hydrogenation of benzonitrile, benzene, and benzylamine are obtained, and from paratolunitrile, a methylbenzylamine, $C_6H_4Me \cdot CH_2 \cdot NH_2$ [Me : CH_2NH_2 = 1 : 4], a colourless oil, resembling trimethylamine in odour, and absorbing carbonic anhydride. Its *hydrochloride* crystallises in flat needles, melting at 234·5—235°; and the *platinochloride* in four-sided tables, sparingly soluble in water. V. H. V.

Constitution of Quinone-derivatives. By A. Hantzsch (*Ber.*, **20**, 1303—1308).—When the sodium salt of quinonedihydroxydicarboxylate is treated with hydrobromic acid until carbonic

anhydride ceases to be evolved, and bromine is added to the product, paradibromodihydroxyquinone, $C_6Br_2(OH)_2O_2$, is formed. This is shown by its physical properties and crystallographic measurements, as also of its sodium and potassium salts, to be identical with bromanilic acid. The rest of the paper is occupied by speculations on the constitution of bromanilic acid; it is suggested that it may be a paradibromotetraketohexamethylene. V. H. V.

Isomeric Chloro- and Bromo-thymoquinones. By K. Schniter (*Ber.*, **20**, 1316—1319).—In the mono-substituted thymoquinones, the positions 3 and 6 are not identical in function, so that according to theory two mono-derivatives are possible. It is remarkable, however, that on addition of the halogen acid to thymoquinone and subsequent oxidation, the same chlorobromothymoquinone is formed whether the chlorine be introduced first and then bromine, or conversely, a result only to be explained by the substitution of different hydrogen atoms by the halogen in the two cases.

α-Chlorothymoquinol, prepared by adding thymoquinone to concentrated hydrochloric acid, crystallises in silky needles melting at 70°, soluble in alcohol and ether.

α-Chlorothymoquinone, prepared by oxidising the above with ferric chloride, was not obtained in a crystalline form.

β-Bromothymoquinol forms colourless needles melting at 53°; it is converted by oxidation into the *quinone*, which crystallises in yellow leaflets melting at 45°.

α-Chloro-β-bromothymoquinol, obtained either from the above α-chloro-derivative and hydrobromic acid, or from the β-bromo-derivative and hydrochloric acid, crystallises in needles melting at 63°; when oxidised it yields the corresponding quinone, crystallising in golden leaflets, and melting at 87°.

β-Chlorothymoquinone, formed from the β-bromo-derivative by substitution, was not obtained in a well-defined condition. The β-chloro-α-bromo-thymoquinone melts at 78°, and the corresponding quinol at 56°. V. H. V.

Substitution of the Amido- by the Nitro-group in Aromatic Compounds. By T. Sandmeyer (*Ber.*, **20**, 1495—1497).—Nitrobenzene is prepared from aniline in the following way:—50 grams of crystallised copper sulphate and 15 grams of grape-sugar are dissolved in 100 c.c. of boiling water and at once treated with a cold solution of 20 grams of soda in 60 c.c. of water. The whole solidifies and then becomes quite liquid; it is quickly cooled and neutralised with acetic acid. 9 grams of aniline, 50 c.c. of water, and 20 grams of nitric acid (sp. gr. 1·4), are mixed, and gradually treated (being kept cool) with a solution of 15 grams of sodium nitrite in 50 c.c. of water; the whole is then added in portions to the solution first prepared contained in a two-litre flask. After two hours, it is distilled, the distillate treated with caustic soda and the nitrobenzene separated. The yield is 5 grams of almost pure nitrobenzene.

Parabromonitrobenzene is prepared in a manner similar to bromo-

benzene from 17 grams of parabromaniline, the amount of nitric acid, &c., being the same as given above; 3 grams of pure product were obtained.

β-Nitronaphthalene is obtained by dissolving 7 grams of β-naphthylamine in a boiling mixture of 15 grams of nitric acid and 250 c.c. of water, cooling quickly, and adding 12 grams of sodium nitrite in 40 c.c. of water. After being treated with the cuprous oxide mixture, it is left for 20 minutes, and treated with alcohol; it is then kept cool for some hours and distilled. The yield of pure β-nitronaphthalene is $\frac{1}{2}$ gram. N. H. M.

Conversion of the Higher Homologues of Phenyl into Amines. By R. Lloyd (*Ber.*, **20**, 1254—1262).—Merz and Weith have succeeded in converting phenol into aniline and diphenylamine by heating it with ammonium-zinc chloride; the conversion is more complete the higher the molecular weight of the phenol. In this paper, the examination of amines obtained from isobutyl- and isoamylphenols, thymol and carvacrol is described. Thus isobutylphenol yields mono- and di-isobutylphenylamine. *Isobutylphenylamine*, $NH_2{\cdot}C_6H_4{\cdot}C_4H_9^{\beta}$, is a brown oil, boiling at 230—231°, its acetyl-derivative crystallises in leaflets, melting at 170°. *Diisobutylphenylamine*, $NH(C_6H_4{\cdot}C_4H_9)_2$, boils at 305—315°; it gives at first a violet, then a blackish-blue coloration with nitric acid; its *platinochloride* crystallises in yellow needles, and its acetyl-derivative in glistening leaflets, melting at 75°, sparingly soluble in water, soluble in alcohol and benzene.

Similarly isoamyphenol yields mono- and di-isoamylphenylamine. *Isoamylphenylamine*, $NH_2{\cdot}C_6H_4{\cdot}C_5H_{11}$, boils at 259—262°. *Diisoamylphenylamine*, $NH(C_6H_4{\cdot}C_5H_{11})_2$, is a thick oil, boiling at 319—321°; its *platinochloride* forms golden-yellow crystals, and its *acetyl-derivative* glistening leaflets, melting at 81°.

From thymol were obtained thymylamine, $NH_2{\cdot}C_{10}H_{13}$, and *dithymylamine*, $NH(C_{10}H_{13})_2$; the latter is an oil of aromatic odour, boiling at 340—345°; its acetyl-derivative crystallises in leaflets, melting at 78°; the former has been investigated by Widman. Of the bases formed from carvacrol, *carvacrylamine*, $C_{10}H_{13}NH_2$, is a colourless oil, boiling at 241—242°, and solidifying at −16°; its *platinochloride* crystallises in prisms, its *acetyl*-derivative crystallises in white tablets melting at 115°, and the *benzoyl*-derivative in rhombic crystals melting at 102°. *Dicarvacrylamine* is a colourless oil boiling at 344—348°, its *hydrochloride* forms a white and the *platinochloride* a yellow precipitate; the *acetyl*-derivative crystallises in scales melting at 78°. In each case numbers are given showing the relative proportions of the primary and secondary base formed according as ammoniacal solutions of zinc ammonium chloride or bromide were used; the bromide gave a better yield than the chloride. The most satisfactory results were obtained in the case of carvacrol. V. H. V.

Dimethylbenzylamine. By C. L. Jackson and J. F. Wing (*Amer. Chem. J.*, **9**, 78—81).—This base has been prepared by

Schotten, but not fully described. *Dimethylbenzylamine* is prepared by the action of benzyl chloride on dimethylamine; the product in aqueous solution is treated with ether, which extracts the substance in question, but leaves dissolved in the water the excess of dimethylamine and also dibenzyldimethylammonium chloride. It boils at 183—184°; its chloride and nitrate are deliquescent; the following three crystalline salts were analysed: $(NMe_2{\cdot}C_7H_7)_2,H_2PtCl_6$, $(NMe_2{\cdot}C_7H_7)_2,H_4Fe(CN)_6$, and $(NMe_2{\cdot}C_7H_7,HCl)_2,ZnCl_2$.

Dimethyldibenzylammonium chloride, $NMe_2(C_7H_7)_2Cl$, prepared as above described, is, after purification, a white crystalline solid, soluble in water and in chloroform; when it separates from aqueous solution it is obtained as an oil, which, however, soon solidifies. Its platinochloride crystallises easily. H. B.

Action of Ethylenediamine on Catechol. By V. Merz and C. Ris (*Ber.*, **20**, 1190—1197).—*Ethyleneorthophenylenediamine*, $NH<\begin{matrix}C_6H_4\\C_2H_4\end{matrix}>NH$, is obtained by heating 3 grams of catechol with 3·2 grams of dried ethylenediamine hydrate at 200° to 210° for 15 hours. The product is treated with cold water, washed with water, and dried over sulphuric acid; it is then distilled in an atmosphere of hydrogen. It crystallises from ether in white, lustrous plates, melts at 96·5—97°, and boils at 287·5—288·5°. It dissolves readily in hot water, warm ether, and in cold alcohol, benzene, and chloroform. When the aqueous solution is heated with ferric chloride, it acquires a blue colour when dilute, violet when more concentrated; on adding hydrochloric acid, the blue colour changes to green or greenish-yellow, and then slowly (on heating quickly) to brown and red. The *oxalate* crystallises in colourless needles, sparingly soluble in alcohol, more soluble in water; it melts at 184° with decomposition. The *picrate* forms a yellow crystalline precipitate, readily soluble in alcohol; it melts just above 120°, with decomposition. When the diamine is oxidised with about five times its weight of potassium ferricyanide, and the product extracted with ether, quinoxaline is obtained. The yield is 64·4 per cent. of the theoretical. The quinoxaline melts at 27·5°, and distils at 225—226° (comp. Hinsberg, *Annalen*, **237**, 333).

Quinoxaline can be reconverted into ethylene orthophenylenediamine by gradually treating the boiling alcoholic solution with sodium; the yield is about 40 per cent. of the weight of the quinoxaline. Other substances are formed in the reaction.

N. H. M.

Nitrophenols and Phenylhydrazine. By A. Barr (*Ber.*, **20**, 1497—1500).—When orthonitrophenol is warmed with phenylhydrazine in presence of xylene as diluent for 1½ hours, orthamidophenol is obtained (comp. Merz and Ris, *Ber.*, **19**, 1754); benzene, ammonia, and nitrogen are formed in the reaction.

Paranitrophenol reacts in like manner with phenylhydrazine; α-dinitrophenol and phenylhydrazine yield benzene and ammonium dinitrophenol. N. H. M.

Thio-derivatives of Diethylaniline and Dimethylaniline. By E. Holzmann (*Ber.*, **20**, 1636—1643).—Sulphur monochloride forms with diethylaniline a *dithiodiethylaniline*, $S_2(C_6H_4{\cdot}NEt_2)_2$; in order to moderate the violence of the reaction, both substances are diluted to a considerable extent with petroleum. The compound crystallises in short, golden prisms, melting at 69—72°; it is sparingly soluble in ether, more readily in alcohol and benzene; it is rapidly decomposed by excess of water. Its *picrate* and *platinochloride* are yellow, amorphous precipitates. By silver nitrate in ammoniacal solution, the sulphur compound is converted into *dioxydiethylaniline*, $O_2(C_6H_4{\cdot}NEt_2)_2$, which crystallises in needles or prisms, melts at 67°, and is decomposed, when moist, in contact with air.

Similarly dimethylaniline reacts with sulphur dichloride to form *thiodimethylaniline*, $S(C_6H_4{\cdot}NMe_2)_2$, which crystallises in pale yellow needles, melts at 123·5°, and is sparingly soluble in warm alcohol and benzene. Its *picrate* and *platinochloride* are similar to those of the above compound, from which, however, it differs in not being convertible into the corresponding oxygen compound. V. H. V.

Sulphazides. By H. Limpricht (*Ber.*, **20**, 1238—1242).—In this paper, several sulphazides are described, a class of substances first investigated by König and Wiesinger, and obtained by passing nitrous acid into an alcoholic solution of the aromatic amines, saturated with nitrous acid.

Metanitrophenylnitrobenzenesulphazide, $C_{12}H_{10}(NO_2)_2N_2SO_2$, is a crystalline powder, melting at 160—162°, soluble in alcohol and acetone, insoluble in water; it slowly reduces Fehling's solution and ammoniacal silver solutions; when boiled with baryta-water, it is decomposed into nitrobenzene and *metanitrobenzenesulphinic acid*, $NO_2{\cdot}C_6H_4{\cdot}SO_2H$. This acid crystallises in glistening needles melting at 95°, and is soluble in ether, sparingly soluble in alcohol; its salts crystallise in prisms.

Paranitrophenylnitrobenzenesulphazide, melting at 160°, resembles the above compound; the corresponding sulphinic acid crystallises in leaflets melting at 120°, and is sparingly soluble in ether.

Orthotolyltoluenesulphazide, $C_{14}H_{16}N_2SO_2$, crystallises in needles melting at 140—142°; its sulphinic acid crystallises in pale-yellow needles melting at 80°.

Nitrotolylnitrotoluenesulphazide crystallises in prisms, melting at 140—142° with decomposition.

The reactions which lead to the formation of these compounds have been previously explained by Königs and Fischer.

V. H. V.

Action of Aldehydes on Phenols. By A. Michael and J. P. Ryder (*Amer. Chem. J.*, **9**, 130—137).—Benzaldehyde and phenol, when heated with a few drops of hydrochloric acid, react with formation of a white, resinous substance, $C_{26}H_{20}O_2$, which yields a white amorphous acetate, $C_{26}H_{18}O_2Ac_2$. Benzaldehyde and pyrogallol, when heated with alcohol and a little hydrochloric acid, yield a white

crystalline substance, to which Baeyer gave the formula $C_{26}H_{22}O_7$, but which is really $C_{26}H_{20}O_6$; it yields a crystalline acetate, $C_{26}H_{14}O_6Ac_6$. Benzaldehyde and phloroglucinol give a resinous compound, insoluble in alcohol; its composition is $C_{26}H_{20}O_6$. Benzaldehyde and orcinol give a white resin of the formula $C_{22}H_{24}O_4$, soluble in alcohol. The behaviour of a number of other phenols and aldehydes was examined; in some cases, a resinous substance was at once formed; in others there was no reaction, even on heating.

A solution of resorcinol in absolute alcohol (1 : 2) with a trace of hydrochloric acid is recommended as a reagent for aldehydes of monobasic acids; if no resin forms after some hours, it is poured into water, when a resinous or a crystalline substance will be precipitated. Ketones give no such reaction, and this reagent is therefore more characteristic than phenylhydrazine or hydroxylamine.

The action of chloral hydrate on resorcinol has been already described (Abstr., 1884, 598); by substituting orcinol for the resorcinol, a more stable product is formed; it can be obtained almost white by recrystallisation, has the formula $C_{23}H_{24}O_8$, and yields an acetate, $C_{35}H_{34}O_{13}$, melting at 185°. The resorcinol compound was again prepared, but it was still found impossible to obtain satisfactory analyses, owing to the ease with which it absorbs oxygen; the acetate is, however, easily obtained pure. When treated with permanganate, it yields a crystalline acid, $C_{20}H_{16}O_8$, which melts at about 210°.

H. B.

Metamethylcinnamic Acid and its Derivatives. By W. Müller (*Ber.*, **20**, 1212—1217).—*Metamethylcinnamic acid*, $C_9H_9{\cdot}COOH$, is obtained by boiling 30 grams of metaxylyl bromide with 35 grams of lead nitrate and 250 grams of water, in a reflux apparatus for 12 hours, a current of carbonic anhydride being passed through the apparatus all the time, in order to carry off the nitrogen oxide formed in the reaction. The product is extracted with ether, the oil so obtained treated with sodium hydrogen sulphite; the white flaky precipitate is separated from the liquid and washed with sodium hydrogen sulphite solution. It is then dissolved in water, separated from the oil which forms, and treated with sodium carbonate. *Metatoluic aldehyde* separates, and is extracted with ether. The aldehyde boils at 199°, and has an odour of benzaldehyde; when exposed to the air, it oxidises very readily to the corresponding acid; 1 part of aldehyde, 1 part of sodium acetate, and 3 parts of acetic anhydride are boiled for eight hours, the product treated with water and with sodium carbonate until alkaline, and steam distilled. The sodium metamethylcinnamate which remains is precipitated with hydrochloric acid, collected, dissolved in a little hot water, and again quickly filtered. It separates in white flakes. It resembles cinnamic acid in appearance, melts at 107·5°, distils with steam, and also alone when quickly heated. The *barium* and *silver salts* form white plates and white flakes respectively; both are almost insoluble. When oxidised with potassium permanganate, the acid is converted into metatoluic acid.

Hydrometamethylcinnamic acid (metamethylphenylpropionic acid),

$C_7H_7{\cdot}C_2H_4{\cdot}COOH$, is prepared by the action of sodium amalgam on metamethylcinnamic acid. It forms white flakes which melt at 40°; it dissolves in water, alcohol, and ether, and distils with steam.

Metamethylcinnamic bromide, $C_9H_9Br_2{\cdot}COOH$, is formed when a solution of metamethylcinnamic acid in carbon bisulphide is treated with a solution of bromine in the same solvent. It melts at 167° with decomposition; it is readily soluble in ether.

Metamethylphenylpropiolic acid, $C_9H_7{\cdot}COOH$, is obtained by boiling the above bromide with alcoholic potash. The product is evaporated, dissolved in water, and precipitated with hydrochloric acid. It melts at 109·5°. When treated with silver nitrate, a white precipitate is formed, which is explosive. When the barium salt is distilled with lime, an oil is obtained (metamethylphenylacetylene), which gives a red precipitate with ammoniacal cuprous chloride solution; this explodes when heated.

Metamethylcinnamene is prepared by leaving powdered cinnamic acid for two or three days in contact with fuming hydrobromic acid. The product is filtered through glass-wool, washed with water, and treated with sodium carbonate. The oil is extracted with ether. It boils at 164°, and becomes solid when kept long.

Metamethylbromocinnamene, $C_7H_7{\cdot}CHBr{\cdot}CH_2Br$, is obtained by the action of bromine on a cooled solution of metamethylcinnamene in chloroform. It melts at 45°.

Metamethyl-α-bromocinnamene, $C_7H_7{\cdot}CH:CHBr$, is prepared by the action of bromine on sodium metamethylcinnamate dissolved in water; it has an agreeable odour, becomes thick when cooled, and boils with decomposition at 242°.

Metamethyl-β-bromocinnamene, $C_7H_7{\cdot}CBr:CH_2$ is prepared by boiling metamethylbromocinnamene with alcoholic potash. It is an oil of an agreeable odour; it cannot be distilled, and blackens at the temperature of the water-bath. N. H. M.

Action of Phosphorus Pentachloride on Salicylic Acid. By J. Chasanowitch (*Ber.*, **20**, 1164—1167).—When the product of the action of phosphorus pentachloride (1 mol.) on salicylic acid (1 mol.) is exposed to air, a solid substance is obtained, readily soluble in water, from which it separates in a crystalline form when kept over sulphuric acid. The compound is monorthocarboxylphenylorthophosphate, $PO(OH)_2O{\cdot}C_6H_4{\cdot}COOH + 3H_2O$, identical with that obtained by Couper (*Annalen*, **109**, 370). The *lead salt*, $(C_7H_4PO_6)_2Pb_3$, and *silver salt*, $C_7H_4PO_6Ag_3$, were analysed. The first product of the reaction is the dichloride, $POCl_2O{\cdot}C_6H_4{\cdot}COCl$ (Anschütz, Abstr., 1885, 1062). The latter distils with partial decomposition into chlorobenzoic chloride. N. H. M.

Homo-orthophthalimide. By S. Gabriel (*Ber.*, **20**, 1198—1205; compare this vol., p. 50).—Dimethylhomophthalimide is best prepared by warming 48 grams of finely powdered homo-orthophthalimide, 50 c.c. of water, 35 grams of powdered potassium hydroxide, and 200 c.c. of alcohol in a flask on a water-bath, until a clear solution is obtained; it is cooled down until lukewarm, and the flask fitted with

a reflux condenser; 87 grams of methyl iodide is gradually added, the whole left for one hour, and then boiled for about three-quarters of an hour. The contents of the flask are evaporated until free from alcohol, treated with hot water, filtered after some hours and then dried and distilled. The distillate is dissolved in soda solution, filtered, and precipitated with ammonia. It is crystallised from a mixture of water and glacial acetic acid (1 : 5). It boils without decomposition at 318·5°, under 770 mm. pressure.

Trimethylhomo-orthophthalimide boils at 294·5° under 770 mm. pressure. The compound $C_9H_4Me_2O_3$ (*loc. cit.*) is best obtained from dimethylhomophthalimide (instead of the trimethyl compound) by digesting it with four parts of fuming hydrochloric acid at 210—220° for four to five hours. When the compound is dissolved in alcoholic potash in presence of a few drops of water, and the solution treated with 5 to 10 volumes of alcohol, and kept in a closed vessel, crystals of the *potassium salt*, $C_9H_4Me_2O_4K_2 + H_2O$, separate. Other salts were prepared. The *free acid*, $COOH{\cdot}C_6H_4{\cdot}CMe_2{\cdot}COOH$, is obtained by dissolving the anhydride in boiling soda, diluting, and supersaturating the cooled solution with hydrochloric acid. It separates in needles of a glassy lustre, soluble in ether, chloroform, and warm water. It melts at 123° when quickly heated, with separation of water. The same decomposition also takes place in hot solutions of the acid containing water.

When the anhydride is distilled with soda-lime, it is converted into isopropylbenzene. The two methyl-groups in dimethylhomophthalimide are therefore attached to the same carbon-atom, as shown in the formula previously ascribed to it (*loc. cit.*).

Homophthalimide sodium, $C_9H_6O_2NNa$, is prepared by adding a solution of 0·23 gram of sodium in 10 c.c. of alcohol to a solution of 1·7 gram of homophthalimide in 80 to 100 c.c. of boiling alcohol; it separates as a yellow, crystalline powder.

Homo-orthophthalaminic acid, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, is formed when benzoylcyanideorthocarboxylic acid (W. Wislicenus, Abstr., 1885, 532) is gradually added to 10 parts of sulphuric acid, and the whole warmed at 70° for half an hour; the product is precipitated by water. It crystallises from boiling alcohol in needles which melt at 185—187°, with evolution of gas; it then solidifies and melts at 230°, the melting point of homo-orthophthalimide. The *methyl salt* of the amido-acid melts at 110—112°.

Benzalhomo-orthophthalimide, $C_{16}H_{11}NO_2$, is obtained by boiling a mixture of homo-orthophthalimide with benzaldehyde for 10 minutes, and treating the product with hot alcohol. It crystallises from alcohol in needles which melt at 173—174°.

Homo-orthophthalimidazobenzene, $C_9H_6NO_2{\cdot}N_2Ph$, is formed when 2·5 grams of homophthalide, dissolved in alcohol, is added to a solution of 5 grams of aniline previously treated with the necessary amount of hydrochloric acid and potassium nitrite to convert it into diazobenzene chloride. It crystallises from glacial acetic acid in orange-coloured needles melting at 258—260°. N. H. M.

Derivatives of Ethyl Quinoneparadicarboxylate. By A. Hantzsch and A. Zeckendorf (*Ber.*, **20**, 1308—1315).—In continuation of the experiments of Hentzsel and Loewy (Abstr., 1886, 354 and 1028), it is shown that the product of the action of chlorine on ethyl dihydroxyquinonedicarboxylate is not represented by the formula $C_5H_6Cl_2O_3$, but by $C_5H_5Cl_2O_3$. The molecular formula should probably be doubled, and the constitution of the compound represented as $C_2O_2(CCl_2{\cdot}COOEt)_2$, *ethyl tetrachlorodiketoadipate*. This view is confirmed by its decomposition by ammonia into 1 mol. of oxamide and 2 mols. of dichloracetamide. The final product of the action of chlorine on ethyl quinonedihydrodicarboxylate and ethyl succinosuccinate is identical, namely, *ethyl dichloroquinonedicarboxylate*, $C_6O_2Cl_2(COOEt)_2$, which crystallises in greenish-yellow needles, melting at 195°; the ready removal of both chlorine-atoms in this compound is remarkable, a change effected even by very dilute aqueous soda. By ammonia, it is converted into *ethyl diamidoquinonedicarboxylate*, $C_6O_2(NH_2)_2(COOEt)_2$, which crystallises in yellow glistening leaflets, decomposed at 270° without fusion; with aniline a *dianilido-derivative*, $C_6O_2(NHPh)_2(COOEt)_2$, is formed, which crystallises in glistening needles melting at 246°; other primary amines give similar products. The above dichloro-compound yields on hydrogenation a compound, $C_{12}H_{12}Cl_2O_6$, probably ethyldichlorodihydroxyterephthalate, which crystallises in grouped needles melting at 123°.

V. H. V.

Direct Conversion of Aromatic Sulphonates into the Corresponding Amido-compounds. By C. L. Jackson and J. F. Wing (*Amer. Chem. J.*, **9**, 75—78).—Although the haloïd organic compounds, with the exception of benzoic chloride, do not act on sodamide or potassamide, yet the corresponding sulphonic acids do. Thus potassium benzenesulphonate fused with sodamide for a short time over a flame gives 10 per cent. of the theoretical yield of aniline; some diphenylamine melting at 53—54° was also formed, probably because the sodamide contained an excess of sodium. Potassium benzenemetadisulphonate in like manner yields metaphenylenediamine, but the yield is much less, amounting only to about 5 per cent.

H. B.

Oxidation of Benzene-derivatives with Potassium Ferricyanide. By W. A. Noyes and C. Walker (*Amer. Chem. J.*, **9**, 93—99).—Orthotoluenesulphonamide, when treated with potassium ferricyanide, yields the corresponding acid (comp. Abstr., 1886, 804), but with other oxidising agents similar substances have yielded sulphinides.

The action of potassium ferricyanide on paraxylenesulphamide is described. The product of the reaction was nearly acidified to precipitate unoxidised paraxylenesulphonamide, evaporated to remove potassium ferrocyanide, then acidified and extracted with ether and the acids converted into barium salts. The mixture of salts extracted with alcohol left barium sulphamineterephthalate insoluble, whilst a barium sulphamineparatoluate passed into solution. The free acid from the barium salts is identical with that described by Remsen and Hall. There appears to be formed also some of the isomeric β-acid.

Sulphamineterephthalic acid, $C_6H_3(COOH)_2 \cdot SO_2NH_2$, was extracted by dissolving the purified barium salt in hydrochloric acid and treating with ether; if, however, the salt is heated with hydrochloric acid, it is converted into hydrogen barium sulphoterephthalate,

$$COOH \cdot C_6H_3 < \begin{matrix} COO \\ SO_3 \end{matrix} > Ba + H_2O.$$

Sulphamineterephthalic acid crystallises easily from hot water, and does not fuse at 310°. The monopotassium salt,

$$COOH \cdot C_6H_3(SO_2NH_2) \cdot COOK + \tfrac{1}{2}H_2O,$$

is sparingly soluble in cold water.

The barium salt ($+H_2O$) when formed by boiling the acid with barium carbonate, dissolves easily, but once separated in the solid condition, it is difficult to redissolve; it forms nodular masses without any well-defined crystalline structure.

For the sake of comparison, terephthalic sulphinide and its barium salt were prepared; the acid potassium salt has been previously described. *Terephthalic sulphinide*, $COOH \cdot C_6H_3 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH$, is easily soluble in hot water, and fuses at 297—299°; it gives a precipitate with silver nitrate almost insoluble in dilute nitric acid; sulphamine-terephthalic acid does not give a similar reaction. The barium salt with $3H_2O$ forms scales very sparingly soluble in water. H. B.

Conversion of β-Naphthaquinone into Indonaphthene-derivatives. By T. Zincke (*Ber.*, **20**, 1265—1272).—In a former paper, Zincke has shown that dichloro-β-naphthaquinone is converted by alkalis into an acid, $C_{10}H_6Cl_2O_3$, which may be regarded as a dichloro-derivative of phenyleneacetyleneglycollic acid,

$$< \begin{matrix} C_6H_4 \\ C_2Cl_2 \end{matrix} > C(OH) \cdot COOH$$

(this vol., p. 54). On oxidation, the acid is converted into a ketone, $< \begin{matrix} C_6H_4 \\ C_2Cl_2 \end{matrix} > CO$, an analogue of diphenylene ketone. These compounds can also be considered as derivatives of indonaphthene, the former as a *dichlorohydroxyindonaphthenecarboxylic acid*, the latter as a *dichloroindonaphthene ketone*. The *ketone* crystallises in yellow, glistening needles, melting at 89—90°, resembling quinone not only in odour, but also in its reactions in that it combines with hydroxylamine and the amines. The hydroxylamine-derivative or oxime,

$$< \begin{matrix} C_6H_4 \\ C_2Cl_2 \end{matrix} > C : NOH,$$

crystallises in needles melting at 120°, the *methylamine*-derivative in dark-red needles melting at 195°, and the *dimethylamine*-derivative in quadratic tablets melting at 140°. These amine-derivatives are decomposed by acids or alkalis with regeneration of the amine and formation of *phenylenechlorohydroxyacetylene ketone*, $C_9H_4ClO \cdot OH$,

which crystallises in leaflets melting at 114°; it is soluble in alkalis with a red coloration, and is converted by phosphoric chloride into a compound, crystallising in leaflets, and differing from the original ketone. It readily takes up chlorine and bromine, yielding colourless, crystalline compounds which no longer possess a quinone character.

V. H. V.

Synthesis of Indonaphthene-derivatives. By W. Roser (*Ber.*, **20**, 1273—1274).—This paper is a preliminary communication with regard to the synthesis of indonaphthene-derivatives from those of cinnamic acid. Thus, dibromocinnamic acid when heated with concentrated sulphuric acid yields *phenylenedibromoacetylene ketone* or *dibromoketoindonaphthene*, $C_6H_4<\begin{matrix}-CO-\\C_2Br_2\end{matrix}>$, crystallising in orange yellow needles melting at 123°. With hydroxylamine, it forms an oxime crystallising in needles melting at 195°, and with aniline an anilide melting at 170°. The ketone combines directly with bromine to form a tetrabromo-additive product, which may be regarded as a derivative of hydrindonaphthene; this compound crystallises in prisms melting at 124°. V. H. V.

Nitrosamines. By O. Fischer and E. Hepp (*Ber.*, **20**, 1247—1253).—In a former paper (this vol., p. 244), it has been shown that the nitrosamines derived from aromatic amines are converted by alcoholic hydrogen chloride into paranitroso-derivatives corresponding with paranitrosodimethylaniline. Thus, from phenyl-α-naphthylnitrosamine a paranitroso-product, $C_{16}H_{12}N_2O$, is obtained, which crystallises in leaflets or needles melting at 150°, and soluble in concentrated sulphuric acid with brown coloration. Similarly from paranitroso-α-dinaphthylamine, a compound, $C_{20}H_{14}N_2O$, is obtained, crystallising in brownish-red needles melting at 169°, and from β-naphthylethylnitrosamine a base, $C_{12}H_{10}N_2$, which crystallises from methyl alcohol in short prisms containing 1 mol. MeOH, melting at 75°. The hydrochloride crystallises in colourless needles, and the platinochloride in yellow needles containing 3 mols. H_2O, the picrate in yellow needles. This substance probably belongs to the anhydro-bases, and its constitution is that of an ethenyl-β-β-naphthalenediamine.

The base obtained from tetrahydroquinolinenitrosamine separates in greenish-yellow flocks, melting at 134°.

It has been observed that the above paranitroso-derivatives dissolve readily in dilute alkalis, and are again reprecipitated on passing in carbonic anhydride. The sodium salt of paranitrosomethylaniline separates in yellow needles of the composition $C_7H_8N_2O + NaOH$, but the formation of such a salt is not in accordance with the formula proposed for those substances by Baeyer and Caro. V. H. V.

Azonium Bases. By O. N. Witt (*Ber.*, **20**, 1183—1186).—Phenylorthonaphthylene-diamine (this vol., p. 590) is prepared by mixing a solution of 10 grams of sulphobenzene-azo-β-naphthylphenylamine in 100 c.c. of alcohol and 10 c.c. of glacial acetic acid, with a solution of 12 grams of stannous chloride dissolved in 20 c.c. of glacial acetic acid. After a short time, pure hydrochloric acid is added until the

red colour of the solution has entirely disappeared. The hydrochloride of the diamine separates in white needles; these are collected and washed with alcohol and ether, and dried at 110°. The base is obtained by treating the alcoholic solution with potash. It forms transparent, flat prisms, which melt at 136—137°, and gradually redden when exposed to air. When dry, it can be heated at 110° without decomposition, but in presence of water it rapidly becomes red.

Phenylnaphthophenanthrazonium nitrate, $C_{30}H_{19}N_3O_3$, is formed when a solution of equal parts of phenanthraquinone and the diamine in glacial acetic acid is boiled for a short time; alcohol and nitric acid (sp. gr. 1·3) are added to the cooled product. It separates after a day in long needles, which are crystallised several times from alcohol; it melts at 110°. The crystals are dichroic. It is almost insoluble in water, but more soluble in alcohol, with a yellowish-red colour. The alcoholic solution when treated with boiling water dyes cotton and wool a salmon colour. The other salts of the base are much more soluble; the *platinochloride* is a red precipitate. The *free base* is soluble in ether; the solution is yellow; it has the constitution $C_{14}H_8\begin{cases}N\cdot C_{10}H_6— \\ NPh(OH)\end{cases}$, and is therefore the analogue of the hypothetical phenylphenazonium hydroxide, of which the author considers saffranine to be the asymmetrical diamido-derivative (*Ber.*, **19**, 3121).

N. H. M.

Azo-derivatives of Phenyl-β-naphthylamine. By T. Zincke and A. T. Lawson (*Ber.*, **20**, 1167—1176).—*Benzene-azo-β-naphthylphenylamine* is obtained by converting 20 grams of aniline into diazobenzene chloride, diluting the liquid with an equal weight of alcohol, and adding it to a warm solution of 47 grams of phenyl-β-naphthylamine in 900 to 1000 c.c. of alcohol. The azo-compound separates in a crystalline form, and after being filtered, washed, and extracted with alcohol, is pure enough for most purposes. It crystallises from hot acetic acid in small lustrous needles of an intense red colour and dark metallic lustre, and melts at 141—142° (not 128—129°; Henriques, Abstr., 1885, 168). When boiled with glacial acetic acid (5—6 parts) and hydrochloric acid (1—1½ part), it is converted into naphthaphenazine, $C_{10}H_6N_2\cdot C_6H_4$, and aniline. This reaction supports the view that the azo-derivatives of β-naphthylamine are hydrazimides; the constitution of benzeneazo-β-naphthylphenylamine would therefore be $C_{10}H_6<\begin{matrix}NPh——— \\ N(NHPh)\end{matrix}>$. Bromine acts on the compound dissolved in warm glacial acetic acid with formation of phenyl-β-naphthylamine tetrabromide, melting at 202—203°; the latter is identical with the compound obtained by Streiff (*Annalen*, **209**, 158).

Amido-β-naphthylphenylamine, $NH_2\cdot C_{10}H_6\cdot NHPh$, is obtained by reducing the azo-compound with stannous chloride. The *hydrochloride* forms long, colourless, lustrous needles, very sparingly soluble in water, more soluble in alcohol; it becomes violet when exposed to air. The *sulphate* resembles the hydrochloride. The

free base crystallises from alcohol in wide needles or plates, which melt at 138—140°, and readily become violet.

Diphenylnaphthaleneazammonium hydroxide, $C_{10}H_6\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle NPh_2\cdot OH$, is prepared by dissolving the azo-derivative of β-phenylnaphthylamine in hot glacial acetic acid (10 parts), heating almost to boiling, and gradually adding to it a hot concentrated solution of potassium dichromate until the solution acquires a brownish-red colour. It is then boiled for a few minutes and diluted with an equal volume of hot water; on cooling, the *chromate* of the base separates in yellow needles. The free base was only obtained in solution; it shows a green fluorescence, precipitates metallic salts, and liberates ammonia. The *chloride*, $C_{22}H_{16}N_3Cl$, crystallises in well-formed lustrous prisms readily soluble in alcohol, less soluble in water. The *platinochloride*, $(C_{22}H_{16}N_3Cl)_2PtCl_4$, forms a crystalline, reddish precipitate sparingly soluble in water; the *sulphate* and *nitrate* form lustrous prisms and long, flat, lustrous needles respectively. The *picrate* crystallises in small needles of an intense yellow colour; it melts at 243°, and is very sparingly soluble in water. N. H. M.

Orthamidoazo- and Hydrazimido-compounds. By T. Zincke and A. T. Lawson (*Ber.*, **20**, 1176—1183).—When a solution of orthodiazoazotoluene (prepared by treating a solution of 5 grams of orthamidoazotoluene in 50 grams of alcohol and 5 grams of strong hydrochloric acid with 1·6 gram of sodium nitrite dissolved in 5 parts of water) is mixed with an alcoholic solution of 3 grams of α-naphthol, and treated with concentrated aqueous soda, a deep red precipitate consisting of the sodium salt of the compound $C_7H_7\cdot N_2\cdot C_7H_7\cdot N_2C_{10}H_6\cdot OH$ is formed. The latter is obtained by decomposing the sodium salt with acetic acid; it crystallises from aniline in brownish-red needles melting at 210°, is sparingly soluble in neutral solvents, but dissolves in dilute alcoholic soda with violet-red coloration. When reduced with stannous chloride in alcoholic solution it yields tolueneazimidotoluene, $C_7H_6:N_3\cdot C_7H_7$, melting at 126°, and amido-α-naphthol hydrochloride together with a small quantity of a substance, probably orthotoluylenediamine.

Orthodiazoazotoluene reacts with β-naphthol with formation of a compound isomeric with that described above. In the case of β-naphthol, the free diazo-compound, and not the sodium salt, separates on the addition of soda. It may be crystallised from chloroform or benzene, when it is obtained in long, deep red prisms of an intense green metallic lustre. It melts at 177°, dissolves readily in chloroform, benzene, and xylene, sparingly in alcohol, acetone, and light petroleum. Alcoholic soda dissolves it only slightly. When reduced, it is converted into the azimide, $C_7H_6:N_3\cdot C_7H_7$, and the hydrochlorides of β-amidonaphthol and para- and ortho-toluidine.

Orthodiazoazotoluene reacts readily with β-naphthylamine with formation of the *compound* $C_7H_7\cdot N_2\cdot C_7H_6\cdot N_2\cdot C_{10}H_6\cdot NH_2$. This crystallises from hot alcohol in deep red, lustrous plates melting at 201—203°; it is readily soluble in chloroform and benzene. When reduced,

it behaves like the naphthol-derivatives, yielding the azimide $C_7H_6 : N_3 \cdot C_7H_7$, and probably also orthonaphthylenediamine; when boiled with hydrochloric acid in alcoholic solution, the azimide is also formed.

The diazo-compounds of paramidoazotoluene are prepared in a manner similar to those of the ortho-compound.

Paradiazoazotoluene nitrate crystallises in slender, brownish-yellow needles, rather readily soluble in water and alcohol; the *perbromide* forms a yellow, crystalline precipitate which changes to slender, violet needles, melting at 96°.

Paradiazoazoimide is obtained by treating the perbromide with an excess of alcoholic ammonia in long, slender, slightly yellow plates melting at 58—60°; it can be crystallised from alcohol, but decomposes when heated or when in contact with sulphuric acid.

When the diazo-salts are reduced with zinc-dust and glacial acetic acid or with stannous chloride, orthotoluidine and orthometatoluenediamine are formed; when sodium sulphite is used, *sodium diazoazotoluene sulphonate*, $C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot SO_3Na$, is obtained; this is a reddish crystalline precipitate, readily soluble in alcohol, sparingly in water.

The diazo-salts combine readily with the naphthols; the *β-naphthol-derivative* forms deep red needles melting at 186°; it is readily soluble in hot alcohol and benzene. When reduced with stannous chloride, it yields β-amidonaphthol, orthotoluidine, and orthometatoluylenediamine.

The diazo-salts of paramidoazotoluene, as well as the perbromide, correspond, therefore, only partially with the compounds of orthamidoazotoluene which yield hydrides when reduced. N. H. M.

Naphtholcarboxylic Acids. By R. Nietzki and A. L. Guitermann (*Ber.*, **20**, 1274—1277).—The naphtholcarboxylic acids are readily decomposed into carbonic anhydride and the corresponding naphthol; in this respect, the β-acid is more unstable than the α-acid. On adding diazobenzene chloride to a solution of α-naphtholcarboxylic acid in dilute alkali, a crystalline precipitate is obtained, but analyses show that it is not homogeneous. On hydrogenation, however, there was obtained an amidonaphtholcarboxylic acid, $OH \cdot C_{10}H_5(NH_2) \cdot COOH$, as a colourless, crystalline powder, decomposing at 230° with evolution of carbonic anhydride. The amidonaphthol obtained from it on oxidation yielded α-naphthaquinone, and thus its constitution was that of a 1 : 4-derivative. Then since the α-naphtholcarboxylic acid is obtained by Kolbe's process from α-naphthol, and in that in the reaction only 1 : 2- and 1 : 4-derivatives are formed, and as the introduced amido-group takes up the second 4-position in the naphtholcarboxylic acid, the OH and COOH groupings are probably in the 1 : 2 positions respectively. V. H. V.

β-Naphthylaminesulphonic Acid. By F. Bayer and C. Duisberg (*Ber.*, **20**, 1426—1432).—*β-Naphthylamine-δ-sulphonic acid*, $NH_2 \cdot C_{10}H_6 \cdot SO_3H$, is prepared by the action of much sulphuric acid on β-naphthylamine at 150° for 1½ hour. The hot solution is poured at

once on to ice, left for some time, and the residue collected and extracted with boiling water several times; it is then further purified by means of the barium or sodium salt. It is sparingly soluble in hot water, and crystallises on the addition of hydrochloric acid to the hot dilute solution of the sodium salt in long, lustrous needles (with 1 mol. H_2O); when boiled for a long time, it separates as a sandy powder (anhydrous). The *barium salt* (with $4\frac{1}{2}$ mols. H_2O) crystallises in groups of slender plates readily soluble in hot water; the *magnesium salt* forms white needles (with 1 mol. H_2O), which show a blue fluorescence. The *sodium* (with 4 mols. H_2O) and *potassium salts* crystallise respectively in small white needles and groups of needles. The acid is distinguished from the α-acid by the solubility of its sodium salt in alcohol, from the β-acid by the solubility of the free acid in boiling water, and from the γ-acid by the sparing solubility of the barium salt. The acid reacts with tetrazodiphenyl with formation of δ-purpurin G, and with tetrazoditolyl chloride with formation of δ-purpurin 5B, a splendid red product.

The δ-acid is formed by heating the pure γ-acid or α-acid with sulphuric acid at 160° for $1\frac{1}{2}$ hour.

β-Naphthol-δ-sulphonic acid is obtained by heating to boiling an aqueous solution of the diazo-compound of β-naphthylamine-δ-sulphonic acid with sulphuric acid, and neutralising with barium carbonate; it is then collected and extracted with sodium carbonate solution. The barium salt is sparingly, the sodium salt readily soluble; the chloride melts at 114° (the chlorides of Bayer's and Schaeffer's acids melt at 61·5° and 135° respectively). The acid is identical with that already prepared by Cassella by heating salts of naphthalene-α-disulphonic acid with alkali. N. H. M.

Purpurogallin. By R. Nietzki and T. Steinmann (*Ber.*, **20**, 1277—1280).—Girard and others have described a substance, purpurogallin, obtained by the oxidation of pyrogallol; a somewhat similar substance, pyrogalloquinone, was obtained by the action of quinone on pyrogallol. In this paper, these two substances are examined, and found to be identical and of the formula $C_{20}H_{16}O_9$; the acetyl-derivative has the formula $C_{20}H_{12}O_9(Ac)_4$. Naphthalene is obtained when purpurogallin is distilled with zinc-dust. V. H. V.

Oxidation of Santonin. By H. Wagner (*Ber.*, **20**, 1662—1665).—Santonin is for the most part unaffected by ordinary oxidising agents; on prolonged treatment with nitric acid, it yields succinic, acetic, and hydrocyanic acids, together with carbonic anhydride; with less complete treatment, oxalic acid is also formed. Other oxidising agents burn only a small proportion of santonin with formation of carbonic anhydride. V. H. V.

Amyrin. By A. Vesterberg (*Ber.*, **20**, 1242—1246).—The crystalline product amyrin, extracted from elemi-resin, has formed the subject of several investigations, but the formulæ assigned to this substance are most discordant. In order to purify the amyrin, it was

converted into the acetyl-derivative; but it was observed that on frequent fractionations of the latter two substances of different crystalline form were obtained, the one, in aggregates of prisms, melting at 235°; the other, in leaflets melting at 220°. The corresponding alcohols, $C_{30}H_{19}\cdot OH$, obtained by hydrolysis, are provisionally called α- and β-amyrin; the former crystallises in delicate needles melting at 180—181°; its *acetate*, mentioned above, melts at 220°, and the benzoate at 192°. When heated with phosphoric chloride, it yields a hydrocarbon, *α-amyrilene* $C_{30}H_{48}$, crystallising in rhombic prisms, $a : b : c = 0{\cdot}667 : 1 : 0{\cdot}4049$, and melts at 134—135°; its specific rotatory power $[\alpha]_D = 109{\cdot}84$ (C = 4).

β-Amyrin melts at 193—194°, its derivatives are less soluble and fusible than those of the α-compounds; its benzoate crystallises in rectangular leaflets melting at 230°. *β-Amyrilene* crystallises in rhombic prisms, $a : b : c = 0{\cdot}916 : 1 : 0{\cdot}540$, melts at 175—178°; $[\alpha]_D = 112{\cdot}19$ (C = 1·515). It is probable that amyrin is allied to cholesterin, and that amyrilene belongs to the class of polymeric terpenes. V. H. V.

Composition of Lac-dye. By R. E. Schmidt (*Ber.*, **20**, 1285—1303).—Before the introduction of the azo-dyes, the lac-dye obtained from lac was a product of some commercial importance; it is produced on the boughs of various trees of the East Indies and Malay Archipelago as an exudation following the puncture by an insect, *Coccus lacca*. The statements in the various technological books are, however, very discordant, and the description of the methods used for the extraction of this dye seems incorrect. From the analytical results obtained with the ash, it would appear that the dye is precipitated from the crude material by the addition of lime, and that the product obtained consists of 10 to 13 per cent. of the dye itself, 9 to 11 per cent. of moisture, 15 to 18 per cent. of mineral constituents, and 57 to 68 per cent. of organic matter and water given off above 100°. A full description is given of the method used to extract and purify the colouring matter; the crystalline substance finally obtained is frequently recrystallised from alcohol and ether. The formula deduced from not very concordant results is $C_{16}H_{12}O_8$, and it is proposed to call the substance *laccaic acid;* it crystallises in microscopic, rhombic tables of a yellowish-red colour soluble in the alcohols, acetone, and acetic acid. Alkalis produce with it a characteristic red coloration, and the changes of tint caused by the addition of various reagents are described in full.

In many of its chemical properties, as also in its absorption spectrum, laccaic acid resembles carminic acid. The salts can only be obtained as amorphous precipitates. When heated with concentrated nitric acid, it yields picric and oxalic acids together with resinous substances, and with hydrochloric acid in sealed tubes it yields, in addition to a gas burning with a green flame, a substance, $C_{26}H_{16}O_{11}$. Laccaic acid when fused with alkali yields two products, the one of phenolic odour volatile in steam, the other contains a non-volatile, crystalline substance, probably an aromatic hydroxycarboxylic acid giving a red coloration with ferric chloride, an acid, probably para-

hydroxymetatoluic acid, which gives no coloration with ferric chloride, and, lastly, a very soluble substance which gives a black precipitate with ferric chloride.

In conclusion, it is noted that laccaic acid and other naturally occurring dyes contain 16 atoms of carbon in the molecule.

V. H. V.

β-Methyltetramethylenediamine and β-Methylpyrrolidine. By H. Oldbach (*Ber.*, **20**, 1654—1659).—On hydrogenation of the nitrile of pyrotartaric acid, *β-methyltetramethylenediamine*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot NH_2$, is formed; it is a colourless liquid boiling at 172—173°, fuming in the air and absorbing water and carbonic anhydride; its *platinochloride* forms small, yellow crystals, the *aurochloride*, prisms; and the *mercurochloride*, small prisms. If the hydrochloride is distilled in small quantities, *β-methylpyrrolidine*, $C_5H_{11}N$, is formed with separation of ammonium chloride; it is best purified by distillation with potash, conversion into the nitroso-derivative, and decomposition of the latter with hydrogen chloride. The free base boils at 103—105°, fumes in the air, and resembles in odour its isomeride piperidine; sp. gr. = 0·8654. Its hydrochloride is very deliquescent; the *platinochloride* crystallises in long prisms, the *aurochloride* in four-sided tables, the bismutho-iodide, $3C_5H_{11}N,HI,2BiI_3$, in red needles. The β-methylpyrrolidine, above described, is not identical with a base found by Brieger in the culture of the *Tetanus bacillus*.

V. H. V.

Action of Amines on Ethylenedibenzoylorthocarboxylic Acid. By J. Baumann (*Ber.*, **20**, 1486—1493).—Ethylenedibenzoylcarboxylic acid is prepared by heating 50 grams of succinic acid, 50 grams of phthalic anhydride, and 17 grams of finely-powdered dry sodium acetate for two hours at 210—220°, breaking up the product and extracting with boiling water, and then several times with boiling alcohol (96 per cent.). The crude ethylenediphthalide is boiled for a few minutes in a reflux apparatus with excess of alcoholic potash (25 grams of substance to 17 grams of potash); the product is treated with water and the alcohol evaporated; more water is added, the whole filtered, and the filtrate carefully treated with dilute hydrochloric acid until a precipitate is formed. It is again filtered and an excess of hydrochloric acid added, when ethylenebenzoylcarboxylic acid separates; this is purified by crystallisation from alcohol. The yield is about 18 grams.

Phenylpyrrolenedibenzoic acid, $NPh<\begin{matrix}C(C_6H_4 \cdot COOH) : CH\\ C(C_6H_4 \cdot COOH) : CH\end{matrix}>$, is obtained by heating 5 grams of ethylenedibenzoylcarboxylic acid with 15 grams of aniline in a water-bath for about half an hour; the product is heated with an excess of hydrochloric acid, filtered, washed with water, extracted, and washed with boiling alcohol. It is crystallised from nitrobenzene, from which it separates in slightly yellow crystals melting at 295° (uncorr.); it is very sparingly soluble in boiling alcohol and glacial acetic acid; rather more soluble in boiling alcohol; insoluble in water, benzene, ether, and chloroform. The *silver salt* forms a white, voluminous precipitate; the *ethyl salt* crys-

tallises in lustrous, yellowish-white needles which melt at 122°; it is readily soluble, except in water.

Ethylpyrrolinedibenzoic acid, $C_{20}H_{17}NO_4$, is prepared by heating ethylenedibenzoylcarboxylic acid with 33 per cent. aqueous solution of ethylamine and some alcohol for one hour at 100°, evaporating the alcohol, and treating with an excess of hydrochloric acid. It is crystallised from dilute alcohol, and forms bright yellow plates melting at 220°, sparingly soluble in ether, benzene, and carbon bisulphide, more soluble in alcohol, nitrobenzene, and glacial acetic acid. The *silver salt* was prepared.

Methylpyrrolinedibenzoic acid, $C_{19}H_{15}NO_4$, prepared in manner similar to the ethyl compound, forms splendid, deep yellow plates, melts at 231°, and resembles the ethyl-derivative in solubility.

Paratolylpyrrolinedibenzoic acid, $C_{25}H_{19}NO_4$, is prepared from ethylenedibenzoylcarboxylic acid (5 grams) and paratoluidine (12 grams); it is purified by dissolving the product in ammonia, filtering, and treating with hydrochloric acid. It crystallises from dilute alcohol in yellowish needles melting at 253°; it is readily soluble.

Diphenylpyrroline, $NH<\begin{matrix}CPh:CH\\CPh:CH\end{matrix}>$, is obtained by distilling pyrrolinedibenzoic acid mixed with lime (20 parts) in a partial vacuum. It crystallises from alcohol in yellowish-white, microscopic needles melting at 143·5°; it is insoluble in water and alkalis, very sparingly soluble in dilute hydrochloric acid (the solution is rose-coloured), readily soluble with red colour in strong sulphuric acid; it is also readily soluble in ether, benzene, &c.

Triphenylpyrroline, $NPh<\begin{matrix}CPh:CH\\CPh:CH\end{matrix}>$, is prepared in a manner similar to the diphenyl compound from phenylpyrrolinedibenzoic acid, using barium oxide instead of lime. It may be recrystallised from glacial acetic acid; it melts at 226°, is almost insoluble in alcohol and ether, sparingly in benzene and glacial acetic acid, and very readily soluble in nitrobenzene and chloroform; it dissolves in sulphuric acid without coloration.

Tolyldiphenylpyrroline, $C_{23}H_{19}N$, is obtained by distilling paratolylpyrrolinedibenzoic acid (2·8 grams) with barium oxide (30 grams). It crystallises from nitrobenzene in groups of bright yellow needles, melts at 201°, dissolves very sparingly in alcohol and glacial acetic acid, is more soluble in benzene and ether, and is readily soluble in nitrobenzene and chloroform.

When 2 grams of ethylenedibenzoylorthocarboxylic acid is heated with 1·3 gram of hydroxylamine hydrochloride, some drops of hydrochloric acid, and 10 c.c. of alcohol for one hour at 100°, long, yellow needles separate which may be crystallised from nitrobenzene. The new compound is the internal anhydride of ethylenebenzoylcarboxylic acid dioxime, and has the constitution

$$CO<\begin{matrix}C_6H_4\\-O\cdot N\end{matrix}>C\cdot CH_2\cdot CH_2\cdot C<\begin{matrix}C_6H_4\\N\cdot O-\end{matrix}>CO.$$

It melts at 270°, and is sparingly soluble except in nitrobenzene.

N. H. M.

The Cinnamene of the Pyridine Series. By A. Ladenburg (*Ber.*, **20**, 1643—1644).—In order to prepare the analogue of cinnamene in the pyridine series, a mixture of ethylene and pyridine was passed through a red-hot tube. Besides subsidiary products not further examined, there was obtained a small quantity of *α-vinylpyridine* as a colourless liquid of pleasant odour boiling at 160°. When oxidised with potassium permanganate, it is converted into picolinic acid, and on hydrogenation with sodium and alcohol into *α*-ethylpiperidine. V. H. V.

Constitution of Aldehydecollidine. By E. Dürkopf and M. Schlaugk (*Ber.*, **20**, 1660—1661).—It is generally assumed that the collidine obtained from aldehyde is an *α*-ethyl-*β*-methylpyridine (Abstr., 1885, 257); subsequent investigations have shown this view to be incorrect. On oxidation, the collidine yields a methylpyridinecarboxylic acid, convertible on distillation with potash into *α*-picoline. It thus becomes necessary to determine the constitution of the dicarboxylic acid obtained as the final product of oxidation of the collidine. V. H. V.

Reactions of Quinolinic Acid. By A. Bernthsen and H. Mettegang (*Ber.*, **20**, 1208—1210).—*Quinolinic anhydride*,

$$C_5NH_3<\begin{matrix}CO\\CO\end{matrix}>O,$$

is readily obtained by the action of acetic anhydride on free quinolinic acid. It crystallises in prisms melting at 134·5°. When heated with resorcinol, *fluorazeïn*, $C_5NH_3<\begin{matrix}C(C_{12}H_8O_3)\\CO—O\end{matrix}>$, is formed which resembles ordinary fluoresceïn.

β-Benzoylpicolinic acid, C_5NH_3·Bz·COOH, is obtained by the action of benzene on quinolinic anhydride in presence of aluminium chloride. It crystallises in prisms which melt at 147°, and is soluble in water. When heated, it is converted, with evolution of carbonic anhydride, into *phenylpyridylketone*, C_5NH_4Bz. The latter boils at 307° (uncorr.). The *phenylhydrazine-derivative* melts at 143·5°. The *platinochloride*, $(C_{12}H_9NO)_2,H_2PtCl_6$, was prepared. The base is converted by oxidation into nicotinic acid. N. H. M.

Quinoline. By. E. Lellman and G. Lange (*Ber.*, **20**, 1446—1451; compare this vol., p. 502).—A mixture of 5 grams of metamidobenzoic acid, 4 to 5 grams of nitrobenzene (better nitrophenol), 20 grams of glycerol, and 25 grams of sulphuric acid, is heated in a reflux apparatus over a free flame until the violent reaction becomes more moderate, when it is kept for six hours at 155—160°. It is cooled to 80°, treated with water, steam distilled, and made alkaline with baryta. It is then filtered, and after the excess of baryta has been removed by means of carbonic anhydride, treated with animal charcoal. The free acid, the yield of which was unsatisfactory, is identical with that obtained by La Coste and Valem by sulphonating quinoline.

When the sodium salt of the sulphonic acid is distilled with potassium cyanide, and the cyanide so obtained is saponified according to Fischer and Körner's method (*Ber.*, **17**, 765), by heating with hydrochloric acid for one day at 140°, a carboxylic acid is obtained identical with that prepared by Lellman and Alt (*loc. cit.*), from metamidobenzoic acid. Hence the sulphonic acid obtained from metamidobenzoic acid belongs to the ana-series, inasmuch as it yields a carboxylic acid having the 4 (ana) position. N. H. M.

Quinoline-derivatives. By L. Rügheimer and C. G. Schramm (*Ber.*, **20**, 1235—1238).—In previous investigations, it has been shown that quinoline-derivatives are formed by the action of phosphoric chloride on salts of malonic acid or its homologues with aromatic amines. Thus from aniline and paratoluidine malonates, trichlorinated quinoline or toluquinoline is produced, and from orthotoluidine malonate a dichlorohydroxytoluquinoline. So, too, from aniline ethyl malonate a *chlorethylhydroxyquinoline*, (Cl : Et : OH = 2′ : 3′ : 4′), is produced. This compound crystallises in colourless needles melting at 248°. As a subsidiary product of the above reaction, a compound, $C_{17}H_{17}N_2O_2Cl$, is formed, which melts at 101·5—104·5°, and is probably an additive product of α-chlorohydroxybutyranilide and phenyl carbamide, both of which substances are formed by heating the compound with sodium carbonate.

Similarly from orthotoluidine, ethyl malonate, and phosphoric chloride, a *chlorethylhydroxytoluquinoline* is produced, which crystallises in glistening, silky needles, melts at 225—225·5°, and is converted by hydrochloric acid into a *hydroxyethyltolucarbostyril*, crystallising in needles and melting at 222—223·5°. V. H. V.

Orthohydroxyquinolinecarboxylic Acid. By R. Schmitt and F. Engelmann (*Ber.*, **20**, 1217—1220).—*Sodium hydroxyquinolinecarboxylate*, $OH{\cdot}C_9NH_5{\cdot}COONa$, is formed quantitatively when sodium quinoloxide and carbonic anhydride are heated in an autoclave for 7 to 8 hours at 140—150°. To obtain the *free acid*, the salt is dissolved in warm, moderately dilute hydrochloric acid; on cooling, hydrochloride of the acid separates in long, lustrous needles. This is filtered and brought into contact with much water, when it gives up the hydrogen chloride, the free acid remaining suspended in the water as a yellow, crystalline mass. When warmed in the slightly acid liquid, it dissolves and separates on cooling in yellow prisms an inch long (with 1 mol. H_2O), the anhydrous substance melts at 235° with evolution of carbonic anhydride and formation of orthohydroxyquinoline, and dissolves sparingly in cold water, alcohol, and benzene; it gives a violet-red to deep-brown coloration with ferric chloride. When the hydrochloride of the acid is boiled with hydrochloric acid and tin, the compound, $OH{\cdot}C_9NH_5{\cdot}COOH,HCl$, is obtained. This crystallises from water in short, thick prisms. The *free acid*, prepared by treating the hydrochloride with the necessary amount of sodium carbonate, forms small, colourless prisms, very sparingly soluble.

Methyltrihydro-orthohydroxyquinolinecarboxylic acid,

$$OH{\cdot}C_9NH_3Me{\cdot}COOH + 2H_2O,$$

is readily obtained by heating the tetrahydro-acid above described with methyl iodide dissolved in methyl alcohol at 120°. The anhydrous acid melts at 211°; it is readily soluble in hot water and in alcohol. N. H. M.

Homologue of Isoquinoline. By S. Gabriel (*Ber.*, **20**, 1205—1208).—8 grams of dimethylhomophthalimide and 24 c.c. of phosphorus oxychloride were heated for 5 hours at 200—210°, the product treated with 4 to 5 vols. of alcohol, filtered after some hours, and washed with alcohol until the product is almost colourless. It is recrystallised from alcohol, from which it separates in long, almost colourless needles, which melt at 165—166°. Analyses point to the formula $C_{11}H_9NCl_2$. The reaction is analogous to that which takes place between homophthalimide and phosphorus oxychloride (this vol., p. 61).

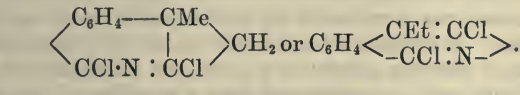
When the compound $C_{11}H_9NCl_2$ is boiled with an equal weight of red phosphorus and 10 parts of hydriodic acid (b. p. 127°), and then distilled with steam, the compound $C_{11}H_{10}NCl$ is obtained. The latter softens at 70° and melts at 78—80°; it is a feeble base.

When 6 grams of the dichloro-compound, 1·4 gram of red phosphorus, and 24 c.c. of hydriodic acid are heated for 3 hours at 200—210°, the product treated with alkali and steam-distilled, an oily and then a clear distillate is obtained, which is heated with 10 c.c. of hydrochloric acid, and then treated with a solution of 4 grams of chromic acid. When cold, it is filtered from the orange-red needles; these are washed and digested with dilute aqueous soda until the red colour has disappeared, when an oil is obtained, which solidifies on cooling. The new base, which has the formula $C_{11}H_{11}N$, melts at 63·5—65° and boils at 274—275° under 763·5 mm. pressure; it has an odour resembling that of quinoline. The *platinochloride*,

$$(C_{11}H_{11}N)_2,H_2PtCl_6 + 2H_2O,$$

forms flat, orange-yellow needles. The *picrate* is sparingly soluble.

The constitution of the dichloro-derivative is probably



N. H. M.

Xanthine-derivatives in Urine. By G. Salomon (*Zeit. physiol. Chem.*, **11**, 410—416).—The presence of hypoxanthine in human urine has been until now a matter of uncertainty. 50 litres of urine was treated with ammonia, and the earthy phosphates filtered off; the filtrate was treated with silver nitrate, and the precipitate washed by decantation, treated with hydrogen sulphide, filtered, and the filtrate evaporated to a small bulk. Ammonia was again added, and the rest of the phosphates removed, silver nitrate again added, and the carefully washed precipitate dissolved in hot nitric acid. On cooling, silver hypoxanthine crystallised out, was purified by recrystallisation, decomposed with hydrogen sulphide, and filtered. On evaporating the filtrate, after adding ammonia, hypoxanthine separated out. This was identified by its reactions, and by elementary analysis.

The xanthine-derivatives of the urine of a dog under the toxic influence of phosphorus was also qualitatively investigated. They were found to be the same as in normal dog's urine. In addition to hypoxanthine prepared in the way above described, heteroxanthine (Abstr., 1886, 266) was also prepared from the mother-liquor from which the silver hypoxanthine had crystallised out. By Weidel's test, an intense red colour was produced. No paraxanthine was present. Hitherto heteroxanthine has been found exclusively in human urine. W. D. H.

The Piperideïne Series. By A. Ladenburg (*Ber.*, **20**, 1645—1647).—The members of the piperideïne series, containing two atoms of hydrogen less than the piperidine series, can be regarded as tetrahydro-derivatives of pyridine. Two bases of the former have been isolated, namely, dimethylpiperideïne and coniceïne; in this paper, other members are described.

Pipecoleïne or *α-methylpiperideïne*, $C_{10}H_{11}N$, is obtained from α-pipecoline hydrochloride by treatment with bromine and sodium, and purification of the base formed by means of its ferrocyanide. It is a liquid boiling at 125—127°, of unpleasant odour; sp. gr. = 0·8801.

α-Ethylpiperideïne, $C_7H_{13}N$, obtained in a similar manner from α-ethylpiperidine, is a liquid boiling at 149—151°, resembling conine in odour, and soluble in water; its salts are very soluble.

α-Isopropylpiperideïne, prepared from isopropylpiperideïne, boils at 163·5°, and is of unpleasant odour; its platinochloride crystallises in tables melting at 189°, with decomposition. V. H. V.

Duboisine. By A. Ladenburg and F. Peterson (*Ber.*, **20**, 1661).—Duboisine is identical with hyoscyamine, as shown by the crystallographic form and melting point of the aurochloride.

Constitution of Tropine. By A. Ladenburg (*Ber.*, **20**, 1647—1654).—The former researches of the author have led to the conclusion that tropine is a tetrahydro-derivative of pyridine, in which one of the hydrogen-atoms is replaced by hydroxyethyl, and another by the methyl group. In order to decide this point, hydrotropidine, $C_8H_{15}N$, is taken as a starting point; this base, on distillation in a current of hydrochloric acid, is converted into a new base, *norhydrotropidine*, $C_7H_{13}N$. The latter is purified by means of its nitroso-derivative, which forms large crystals, melting at 116—117°, readily soluble in benzene and ether, and decomposed by hydrochloric acid, with formation of the free base; this is a colourless, transparent, crystalline substance, boiling about 161°, but not of very definite melting point. The hydrochloride melts at 281°, with decomposition, and the platinochloride crystallises in prisms, which carbonise above 225° without fusion. A solution of the hydrochloride gives precipitates with auric and mercuric chlorides and picric acid. Norhydrotropidine on distillation with zinc-dust, yields a base, shown to be identical with α-ethylpyridine. Tropine is therefore a hydroxyethylmethylpyridine, $C_5NH_7Me{\cdot}C_2H_4{\cdot}OH$, a formula to be preferred to that, $OH{\cdot}C_5NH_6EtMe$, proposed by Fischer as bringing out the analogies of tropine with

neurine and the triacetonalkamines. Further, the ethyl group, as such, is seldom present in naturally occurring substances.

V. H. V.

Ecgonine. By A. Einhorn (*Ber.*, **20**, 1221—1229).—*Anhydroecgonine*, $C_9H_{13}NO_2$, is prepared by boiling ecgonine hydrochloride (20 grams) with phosphorus oxychloride (100 grams) for two hours in a reflux apparatus. The product is poured into water, converted into periodide (by adding a solution of iodine in hydriodic acid), filtered, washed with water, and steam-distilled. Iodine is given off, and anhydroecgonine hydrochloride remains. The latter is recrystallised from absolute alcohol, dissolved in water, and treated with silver oxide. It is purified by precipitation from its alcoholic solution with ether. It is a colourless, crystalline substance melting at 235° with evolution of gas; it dissolves very readily in water and alcohol, and is almost insoluble in ether, chloroform, benzene, and light petroleum. The *hydrochloride* is obtained by treating the hydriodide with silver chloride; it crystallises from absolute alcohol in compact, white needles which melt at 240—241°. The *platinochloride* forms yellowish-red prisms melting at 223° with decomposition. The *aurochloride* (Merck, this vol., p. 284) forms sulphur-coloured prisms. The *hydrobromide* is orange-coloured, and melts at 154—155° with decomposition. The periodide, $C_9H_{13}NO_2,HI,I_2$, crystallises from glacial acetic acid in brownish-violet plates melting at 185—186°. It gives up its iodine in presence of sulphurous acid, ammonia, and mercury.

Anhydroecgonine forms salts with bases; the *sodium salt* was prepared. *Ethyl anhydroecgonine*, $C_9H_{12}NO_2Et$, is obtained by passing dry hydrogen chloride through a solution of anhydroecgonine hydriodide in absolute alcohol. It forms an oil. It dissolves very readily in hydrochloric acid, yielding a compound crystallising in needles; it melts at 243—244°. The *platinochloride*, $C_9H_{12}NO_2Et,H_2PtCl_6$, forms yellow prisms melting at 211°. The *perbromide* is very unstable. The formation of this ether points to the presence of a carboxyl-group in anhydroecgonine. This and the fact that a dilute aqueous solution of anhydroecgonine decolorises potassium permanganate, whilst ecgonine does not, makes it probable that anhydroecgonine contains the group —CH : CH : COOH. This view is confirmed by the formation of a *bromide* isomeric with the perbromide already mentioned, but more stable. The latter is obtained by heating anhydroecgonine hydrobromide with a slight excess of bromine for 1½ hours at 100°. It melts at 165° with decomposition. *Anhydroecgonine dibromide hydrochloride*, $C_8H_{12}NBr_2{\cdot}COOH,HCl$, is readily obtained by heating 1 gram of anhydroecgonine hydrochloride with 2·5 grams of bromine dissolved in glacial acetic acid for two hours at 100°. It crystallises from alcohol in prisms which melt at 183—184°. When bromine is added to an aqueous solution of anhydroecgonine hydrochloride, *anhydroecgonine hydrobromide perbromide* is formed; it crystallises from glacial acetic acid in orange-coloured needles which melt at 154—156°. The hydrochloride of the perbromide appears not to exist. When the product of the action of bromine on anhydroecgonine hydrochloride and the bromide, melting at 165°, are treated with sodium carbonate, an oil is obtained having the properties of a compound corresponding

with bromo-α-cinnamene. The presence of an acrylic acid group is thus proved. Merck (*loc. cit.*) has shown that both ecgonine and also anhydroecgonine contain a methyl group attached to nitrogen; anhydroecgonine is therefore tetrahydropyridylacrylic acid,

$$C_5NH_7Me\cdot CH\cdot CH\cdot COOH;$$

ecgonine is methyltetrahydropyridyl-β-hydroxypropionic acid,

$$C_5NH_7Me\cdot CH(OH)\cdot CH_2\cdot COOH;$$

cocaïne is methylic methyltetrahydropyridyl-β-benzoylhydroxypropionate, $C_5NH_7Me\cdot CH(OBz)\cdot CH_2\cdot COOMe$. N. H. M.

Ptomaïnes from Pure Cultivations of "Vibrio Proteus." By O. Bocklisch (*Ber.*, **20**. 1441—1446).—Finkler's bacillus decomposes beef with formation of ammonia and cadaverine which was isolated, the picrate prepared and analysed. Choline and creatinine are present in the fresh beef.

Beef was kept in contact with *Vibrio proteus* mixed with some putrefactive bacteria which always accompany it when in the forward intestines. Creatinine and methylguanidine were obtained together with a small amount of cadaverine.

Cadaverine has all the properties of pentamethylenediamine (Ladenburg, this vol., p. 125), except that the mercurochloride of pentamethylenediamine contains 3 mols. $HgCl_2$, whilst that of cadaverine has 4 mols. The author prepared and analysed the latter compound, and obtained numbers pointing to the formula with 4 mols. $HgCl_2$.

Cadaverine oxalate, $C_5H_{14}N_2,H_2C_2O_4 + 2H_2O$, is obtained by mixing the cadaverine base with oxalic acid dissolved in alcohol; it crystallises in needles which melt at about 160° with evolution of gas. When treated with an alcoholic solution of oxalic acid, the *salt*, $C_5H_{14}N_2(H_2C_2O_4)_2 + H_2O$, is obtained. This crystallises in quadratic plates which melt with decomposition at 143°. N. H. M.

The Acids of Pig's Bile. By S. Jolin (*Zeit. physiol. Chem.*, **11**, 417—420).—In addition to the well-known hyoglycocholic acid first obtained by Strecker from pig's bile, a small quantity of another acid, β-hyoglycocholic acid, is also present. The two acids can be separated by the use of sodium sulphate, which readily precipitates Strecker's α-acid, but not the β-acid. By the use of an ice-cold saturated solution of sodium sulphate, which contains less salt than a warm one, the α-acid is precipitated, and the β-acid remains in solution. When this solution is concentrated by heat, the sodium salt of the β-acid separates in the form of oily drops of a dark brown colour; on cooling these set to a sticky mass. It is soluble in alcohol, and can be freed from fat, cholesterin, and pigment by ether. It is then a white, curdy substance, easily soluble in alcohol and in water; it is incompletely precipitated by saturating the aqueous solution with sodium sulphate. With barium salts, a barium compound is formed which precisely resembles that obtained from the α-acid. The acids themselves are both insoluble in water, and behave to most reagents in a similar way; the β-salts, as a rule, melt more easily, and their

taste is less bitter than that of the α-salts. Both give Pettenkofer's reaction. The cholic acid from both has the same properties. The nitrogen of the two acids is about equal in amount. The carbon is rather less in the β-acid than in the α-acid; but on account of the difficulty of crystallising the compounds of the β-acid, it is not easy to make trustworthy analyses. W. D. H.

Physiological Chemistry.

Absorption in the Stomach of the Horse. By H. Goldschmidt (*Zeit. physiol. Chem.*, **11**, 421—437).—The amount of absorption which takes place from the stomach is difficult to estimate accurately, especially because it is difficult to make allowance for the composition and particularly for the proteïd constituents of the various digestive juices. The result can only be taken as comparative, and not absolutely correct. The general method of the analysis may be seen from the following example:—Horse killed 1½ hours after food; the stomach contained 120·17 grams of cellulose, which correspond with 1442·6 grams of oats which contain 142·24 grams of proteïd and 924·562 grams of constituents free from nitrogen, and about 200 grams of water. In the stomach, 3200 grams of juice was present which, deducting the 200 grams of water in the oats, leaves 3000 grams as the weight of saliva and gastric juice; 3000 grams of saliva contain 0·548 per cent. of proteïd—that is about 16·4 grams in all. In the stomach, the analysis of the contents gave the following results:—

	Proteïd.	Substances free from nitrogen.
Undigested.....	67·35 grams	652·48
In solution	43·00 ,,	125·31
Total in stomach....	110·35 ,,	777·79
In oats and saliva ..	158·64 ,,	924·562
Absorbed.....	48·29 ,,	146·772
	or 34 per cent.	or 16 per cent.

Eight similar investigations were made in which the general results may be tabulated as follows:—

Horse.	Hours killed after death.	Percentage of proteïds absorbed.	Percentage of non-nitrogenous substances absorbed.
No. 1.	1½	34	16
,, 3.	2½	19	13
,, 4.	3½	39	28
,, 5.	4½	29	23
,, 6.	6½	49	43
,, 7.	8	64	51
,, 8.	10	64	59
,, 9.	12	61	51

In the horses numbered 1, 4, 7, absorption was great; and in those numbered 3, 5, 6, 8, and 9, not so marked: this corresponds with the activity of digestion in the individual cases. The greatest part of the digested non-nitrogenous stuffs and an important part of the nitrogenous are absorbed during and after the sixth hour after food.

On account of the difficulty in these estimations arising from the want of knowledge concerning the composition of the digestive juices, some analyses were made to serve as data on which to correct the first series of observations; the various juices in the stomach, the duodenum, the middle of the small intestine, the ileum, the cæcum, the ventral colon, and the dorsal colon were investigated in two horses A and B. The percentages of proteïds were as follow:—

	Stomach.	Duodenum.	Jejunum.	Ileum.	Cæcum.	Colon.	
						Ventral.	Dorsal.
A.	0·594	1·567	1·006	0·594	0·854	—	—
B.	1·238	5·088	1·856	1·675	0·656	1·476	1·638

The following conclusions are drawn:—

1. That the intestinal juice becomes poorer in proteïds, non-nitrogenous constituents, total solids, and ash towards its ileal end.

2. That the amount of water correspondingly increases.

3. That the proteïds throughout are present in important quantities.

Somewhat similar investigations by Ellenberger and Hofmeister (*Archiv. f. prakt. u. Wissensh. Thierheilkunde*, **10**, 328) in three horses gave an average result closely corresponding with that obtained in horse A. W. D. H.

Digestion and Digestive Secretions of the Horse. By Ellenberger and Hofmeister (*Bied. Centr.*, 1887, 229—232).—This is a review of the long researches of the authors on this subject, of which many abstracts have been given in this Journal, and in the course of which many interesting particulars relating to the digestion of vegetable substances by men and animals have been treated.

The action of saliva in the process of mastication is shown to be more mechanical than chemical. The quantity of saliva used depends on the dryness and roughness of the food rather than its contents in starch, and the authors think that the chemical activity of saliva owes much to spores, which floating in the atmosphere, mix with the food and assist in the fermentation process.

A digestive action of the mixed food takes place in the stomach when the acidity due to hydrochloric or lactic acid does not exceed 0·03 to 0·04 per cent. The left section of the stomach of the horse does not secrete a gastric juice, this is the function of the right portion. The pure gastric fluid of the horse contains lactic, fatty, and amylaceous ferments, the latter in small quantities.

Cellulose is not digested in the stomach of the horse, but muscle, fat, gelatin, and flesh generally are easily digested, bone and elastic tissues more slowly. Pepsin operates actively only when acids are present, about 2 per cent. of lactic acid or 0·2 per cent. of hydrochloric acid being necessary; the activity of pepsin does not increase in proportion to its quantity after reaching a certain point, but it rather becomes injurious.

The acid which appears first in the digestive process is lactic acid and later hydrochloric; at the time of greatest activity, lactic acid is present in the upper and lower extremities of the digestive tract, hydrochloric acid being found in the intervening part.

The digestion of starch in the stomach of the horse lasts for about two hours, that of albuminous matter takes place later, and occupies three or four hours after the eating of the food; the drinking of water immediately after food does not appear to hinder digestion.

The secretions of the intestinal canal unite in themselves all the properties of the gastric juice, and can act as a substitute for it, and are particularly energetic in the decomposition of fats.

The duration of the digestive process in the horse is long, lasting almost three days.

A very active lactic fermentation of sugar takes place in the stomach and intestines, but the authors do not say that all the sugar which is lost in the course of passage is lost in that way, it is more probably reabsorbed. J. F.

Changes in Milk produced by Freezing. By Kaiser and Schmieder (*Bied. Centr.*, 1887, 267—269).—The matter is of importance to milk dealers in cold countries, where the contents of their cans become frozen.

Two samples were experimented with, one was frozen slowly, the other quickly, and afterwards partially thawed, in the former case the ice contained the greater part of the fat and the fluid portion most of the caseïn, milk-sugar, and salts.

In the quickly frozen and partially thawed sample, the fat was equally distributed between the solid and fluid portions; the author explains this by the fat globules rising to the top when the process of freezing is gradual, they thus become imbedded in the flakes of ice, whilst in quickly frozen samples this cannot take place, and the fat is more evenly distributed.

If a dealer whose milk has been frozen pours off the clear fluid which underlies the ice, he is liable to the suspicion of adulteration on the one hand, or will deliver milk above the standard on the other. Milk which has been frozen should be well thawed and shaken up, and not sold whilst any ice is visible. J. F.

Frozen Milk. By O. Henzold (*Bied. Centr.*, 1887, 269—270).—The experiment shows different results, as in the quickly frozen sample, the ice contained a much larger proportion of fat than the ice of the slowly frozen, but the *modus operandi* was different, as during the process of slow freezing the milk was frequently agitated. J. F.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Sugar by Elliptical Yeast. By E. Claudon and E. C. Morin (*Compt. rend.*, **104**, 1109—1111).—The yeast was obtained from a white wine of Rouillac, and was purified by successive cultivations. Fermentation took place at a temperature of 18—20°, and foreign germs were excluded. On distillation, the product was separated into an alcoholic liquid, an acid liquid, and a residue consisting of glycol, glycerol, and non-volatile products. The products from 100 kilos. of sugar were as follows—

Aldehyde	traces.
Ethyl alcohol	50615·0 grams
Normal propyl alcohol	2·0 ,,
Isobutyl alcohol	1·5 ,,
Amyl alcohol	51·0 ,,
Ethyl œnanthylate	2·0 ,,
Isobutylene glycol	158·0 ,,
Glycerol	2120·0 ,,
Acetic acid	205·3 ,,
Succinic acid	452·0 ,,

The proportion of propyl and isobutyl alcohols is unusually low, and amyl alcohol constitutes almost the whole of the higher alcohols. The bases usually present in fusel oils are absent, and so also are normal butyl alcohol and butyric acid, which were found by Ordonneau in brandy (Abstr., 1886, 436). C. H. B.

Formation of Nitrogen during Putrefaction. By A. Ehrenberg (*Zeit. physiol. Chem.*, **11**, 438—471).—This research follows up the author's previous observations (this vol., p. 172), and is devoted to the question as to whether free nitrogen is formed during the processes of nitrification induced by low organisms. The apparatus previously described was used. Earth containing the necessary organisms was added to a 2 per cent. solution of ammonium chloride, to a mixture of calcium sulphate, calcium carbonate, and ammonium chloride, in the presence of pure oxygen, and to a mixture of peptone, sodium chloride, sodium phosphate, saltpetre, and cane-sugar, in the presence of carbonic anhydride; but in none of these instances was any nitrogen given off, nor was nitric acid formed. In other experiments, in which putrefactive processes were more intense, in which urine, fæces, blood, and other organic matter was used and in which there was formation of nitrates, free nitrogen was formed as well; the details of the several experiments are given. In the absence of oxygen, and also in the presence of a large quantity of this gas, free nitrogen is not formed; in the first case, methane and carbonic anhydride, and in the latter case carbonic anhydride alone are the gaseous products. In cases where nitrates and free nitrogen are formed, there is also at first a formation of methane.

W. D. H.

Absorption of Aniline Colours by Living Cells. By W. Pfeffer (*Ann. Agronom.*, **13**, 176—179).—The author has worked with very dilute solutions (1 in 100,000 or 1,000,000) of methylene-blue, methyl-violet, Bismarck-brown, magenta, &c., with a view of throwing light on the accumulation of such substances as sugar, nitre, &c., in particular organs of plants. The results show that the protoplasmic layer of living cells behaves very differently towards these colouring matters under different circumstances. Some colours are absorbed, some are not; those which are absorbed generally accumulate in the cell sap; all colour the protoplasmic layer in traversing it, except methylene-blue. Arriving in the cell sap, the colouring matter may behave in three different ways; it may accumulate in solution, may form a precipitate, or may attach itself to a pre-formed substance, generally tannic acid. In *dead* cells, the colour is absorbed by the nucleus. J. M. H. M.

Presence of Choline in Germinating Plants. By E. Schulze (*Zeit. physiol. Chem.*, **11**, 365—372).—Employing Brieger's method for the separation of nitrogenous bases, it is possible to obtain choline from germinating pumpkin sprouts. The base was identified by its reactions, and by the characters and elementary composition of its aurochloride and platinochloride. The quantity present is very small; from a kilogram of the dried sprouts, only about 3 grams of the aurochloride was obtained. W. D. H.

Composition of Potatoes. By M. A. Scovell and A. E. Menke (*Amer. Chem. J.*, **9**, 103—107).—The following numbers are the maxima and minima obtained in the analyses of 20 varieties of potatoes:—Specific gravity, 1·0923—1·0731; dry substance, 22·91—20·20; starch, 16·05—12·05; sugar, gum, &c., calculated as glucose, 1·49—0·74. The specific gravity cannot be used for calculating the percentage of starch. The addition of various fertilisers has no appreciable influence on the proportions of the various constituents. The albuminoïds are most readily acted on by dilute hydrochloric acid; the percentage of albuminoïds varied from 2·19 to 2·69, that of peptones from 0·0294 to 0·0418: tyrosine formed about 0·008 per cent.; leucine and asparagine were not estimated. H. B.

Effects of Deep or Shallow Sowing on Cereals. By E. Stössner (*Bied. Centr.*, 1887, 236—244).—The author has been making experiments in sowing the seeds of wheat, rye, barley, and oats at different depths, and gives a *résumé* of his conclusions, from which the following are selected:—

The depth at which the seed is sown is of great importance, an improper depth reducing the weight of the crop sometimes by one-half.

In loamy humous soils, both winter and summer wheat, rye, and oats should not be sown deeper than 4 cm., whilst summer barley will bear a covering of 10 cm. When a large yield of straw is desired, the seed may be planted at a greater depth than when the heaviest grain crop is desired. In good soil, well pulverised and rolled, the

covering may be only 2 cm. provided it is retentive of moisture. Seeds should, if possible, be procured from the previous year's crop, and never used when over two years old.

There are other recommendations well known in agricultural practice. J. F.

Manurial Experiments with Sugar-beets. By A. Pagnoul (*Bied. Centr.*, 1887, 223—227).—The experiments were made in vessels containing about 1200 litres filled with a sand freed from lime and organic matter, but containing traces of alumina, iron, phosphoric acid, and potash.

The manures employed were Chili saltpetre (15·5 per cent. N), ammonium sulphate with 20 per cent. N, ammonium nitrate, and dried blood; potassium chloride 50 per cent.; superphosphate; Thomas slag with 7 per cent. phosphoric acid, and finely ground natural phosphate of 20 per cent., with addition of carbonate of lime.

The growth of the beets sown without any manure, and those manured without phosphoric acid was slow and weak. The ground raw phosphate and the Thomas slag produced very good effects, and the addition of carbonate of lime increased the crop in every case. The best results were obtained from a mixture of 600 parts of Chili saltpetre, 600 of superphosphate, and 300 of potassium chloride, and with another mixture of 500 parts of dried blood, 300 Chili saltpetre, 300 calcium chloride, 660 superphosphate, and 1000 carbonate of lime.

The average weight of the roots, however, shows that sand to which is added theoretically correct quantities of manures, does not produce as favourable results as natural soils.

One of the vessels was manured with crushed oil-cake placed at a certain distance from the seeds. The plants were longer in developing, but the crop of leaves was as large as in the case of the complete manure, the roots attained an abnormal length, and they passed in a slanting direction so as to reach the oil-cake, which was not thoroughly mixed with the soil as in the case of soluble manures. The sugar contents of the juice was considerably influenced by the nature of the manure; the absence of potash sensibly diminished the yield of sugar, and in one case where both soda and potash were absent the actual weight of the whole roots was diminished one-half. Soda appears to have more affinity for organic salts than potash, and forms larger quantities of those salts which are considered impurities of beet-juice. It is also shown that when manured with substances containing both soda and potash, the latter is absorbed in preference to the former. J. F.

Analytical Chemistry.

Weil's Method for Determining Sulphur. By C. Friedheim (*Ber.*, **20**, 1483—1485).—The author made determinations of sulphur by Weil's method, and obtained results which confirm the statement previously made by him (this vol., p. 396) that a correct result can only be obtained when the error in one direction happens to equal that in the other. This remark applies to the results since given by Weil (this vol., p. 618). N. H. M.

Detection of Sulphites in Presence of Thiosulphates and Sulphates. By A. Villiers (*Compt. rend.*, **104**, 1177—1178).—When a solution of a normal alkaline sulphite is mixed with excess of barium chloride, barium sulphite is precipitated, and the liquid which was originally strongly alkaline becomes neutral to litmus. If the barium chloride is added to an alkaline hydrogen sulphite, normal barium sulphite is precipitated, and free sulphurous acid remains in solution. A solution which contains a mixture of a normal alkaline sulphite and a hydrogen sulphite has a distinctly alkaline reaction even when the proportion of normal salt is very small, but after addition of barium chloride the solution becomes acid and contains free sulphurous acid.

To detect sulphites in presence of thiosulphates, the solution is neutralised with hydrochloric acid, care being taken to avoid excess, and the liquid is mixed with barium chloride, when its reaction becomes acid to litmus. If the liquid is distilled, the sulphurous anhydride passes over with the first portion of the distillate, and can be detected in the usual way. The filtered liquid can also be tested for sulphurous acid by means of iodine, without distillation.

This method is also applicable in presence of the thionic acids.

C. H. B.

New Method for the Quantitative Determination of Hydroxyl. By C. L. Jackson and G. W. Rolfe (*Amer. Chem. J.*, **9**, 82—87).—As an improvement on the ordinary method of determining hydroxyl groups in organic compounds, parabromobenzoic chloride or anhydride is substituted for acetic or benzoic chloride, and in the ethereal salts formed with the compound in question, the bromine is estimated by Carius' method. The differences to be looked for are almost twice as great as in the analyses of the acetyl or benzoyl compounds, and the parabromobenzoyl compounds are easily prepared and purified.

The method of preparing parabromobenzoic acid is described; the yield amounts to 40—70 per cent. *Parabromobenzoic chloride*, $C_6H_4Br{\cdot}COCl$, has been previously prepared, but not described. It melts at 30°, and boils at 245—247°; it is not dissolved or acted on by cold water, but dissolves in benzene and in alcohol, being then converted into its ethereal salt. *Parabromobenzoic anhydride*,

$$(C_6H_4Br{\cdot}CO)_2O,$$

is very insoluble in ordinary reagents, is crystalline, and melts at 212—213°. Its best solvent is chloroform.

Parabromobenzamide, $C_6H_4Br\cdot CONH_2$, was prepared from the chloride, it is nearly insoluble in cold water, is crystalline, and melts at 186°.

As an example of the application of the method, the preparation of the two following compounds is described. *Phenyl parabromobenzoate*, $C_6H_4Br\cdot COOC_6H_5$, was obtained by heating at about 200° phenol, with either parabromobenzoic chloride or anhydride. It forms crystals resembling naphthalene, melting at 117°, insoluble in water, but soluble in other solvents. *Pyrogallol triparabromobenzoate*, $(C_6H_4Br\cdot COO)_3C_6H_3$, was made by heating pyrogallol with the chloride at 100°; the excess of chloride was removed by light petroleum and the pyrogallol by sodium carbonate. The substance crystallises easily from hot benzene, and melts at 140°. The corresponding pyrogallol tribenzoate is resinous, and hardly capable of purification.

H. B.

Quantitative Estimation of Glycerol. By R. Diez (*Zeit. physiol. Chem.*, **11**, 472—484).—The methods hitherto employed for the estimation of glycerol in wine and beer consist in dissolving it out usually by alcohol and ether from a mixture of the beverage with chalk, and finally weighing the glycerol. Neubauer and Borgmann (Abstr., 1879, 404) found that the glycerol so obtained contained 2 per cent. of mineral constituents and 0·4 per cent. of nitrogen. Champion and Pellet (this Journ., 1873, 1165) devised a method in which the glycerol was obtained as nitroglycerol, and weighed in this form, but this and other methods are also liable to error. The present method is one in which the compounds of glycerol with benzoyl are weighed. There are three benzoates of glycerol, according as to whether one, two, or three atoms of the hydrogen of the latter are replaced by the group $C_7H_5O_2$. The following gives the method of procedure:—Glycerol was diluted to a known extent with water (0·1 gram in 10 or 20 c.c.); 5 c.c. of benzoic chloride and 35 c.c. of sodium hydroxide added; this mixture was cooled and shaken for 10 to 15 minutes. The benzoyl compound which separated was collected on a weighed filter, washed with water, dried at 100°, and weighed. A mean of eight estimations gave the amount of the compound as 0·385 gram. In a second series of four estimations, the number obtained was rather higher, the mean being 0·395 gram; in these cases, the alkaline filtrate was shaken a second time with benzoic chloride and sodium hydroxide; the second filtrate contained hardly a trace of glycerol. These numbers formed a basis for the subsequent analyses, and showed that the compound formed in this way was chiefly the tribenzoate; theoretically the amount of that compound for 0·1 gram of glycerol would be 0·439 gram. Tables of the amount of glycerol in various forms of beer and wine, estimated by this method, are given, the numbers obtained being somewhat less than those given by Borgmann. The method has the following advantages: the substance weighed is solid and not hygroscopic, and admixture with inorganic and nitrogenous substances is avoided.

W. D. H.

New Sugar Reactions. By D. Lindo (*Chem. News*, **55**, 230 and 239).—With reference to the new reactions for sugar described by Molisch (Abstr., 1886, 923), the author has found that a 1 per cent. starch or gum solution gives this reaction with thymol, as does also one part of cane-sugar in 200,000 of distilled water, and that all samples of normal human urine do so also, even when diluted with 50 vols. of water. He considers, however, that this fails to prove the presence of sugar is normal urine, which as a complex fluid must be acted on by the sulphuric acid. He finds that nitrates give the same characteristic colour reactions and precipitate on dilution, and that similar results are obtained when menthol is substituted for thymol; menthol has also the advantage of not giving with nitrates or nitrites any reaction that could be mistaken for that of sugar. Chlorides or hydrochloric acid do not impair the delicacy of either test, but sugar cannot be detected by either, in the presence of notable quantities of nitrates or nitrites. R. R.

Analyses of Sugar-cane and Beet Juices. By C. A. Crampton (*Chem. News*, **55**, 207—209).—The paper details the author's method of analysing sugar juices. By working with a smaller quantity and using the same solution, first for polarisation and then for reduction by Fehling's solution, with filtration by means of Wiley's tubes, he is enabled to expedite the process. The paper contains an extended table for calculating the results from the different factors obtained. R. R.

Separation of Acetic Acid from Formic Acid. By D. S. Macnair (*Chem. News*, **55**, 229).—For the quantitative estimation of acetic acid in presence of formic acid, the author recommends that the substance be distilled with dilute sulphuric acid, and the distillate boiled for 10 minutes in a reflux apparatus, with an equal bulk of chromic acid mixture, made by dissolving 12 grams of potassium dichromate in 30 c.c. of sulphuric acid, diluted with 100 c.c. of water. Acetic acid only remains unchanged, and when the liquid is distilled, passes over and can be titrated in the distillate. R. R.

Analysis of Milk. By F. G. Short (*Amer. Chem. J.*, **9**, 100—103).—About 2 c.c. of the milk is weighed into a very thin, tared glass capsule, containing a quantity of asbestos, and dried at 110° for two hours. For the determination of the fat, the capsule is wrapped in a piece of cheese cloth, crushed and pushed tightly into the tube of a continuous ether extraction apparatus, and extracted for two hours with 50 c.c. of ether; the ether then evaporated, and the flakes heated in the drying oven for three hours before weighing. The same method can be used for butter analysis; the sample is placed in a jar or bottle, the whole melted and then vigorously shaken until solid. The drying and extraction of fat is carried out as before. In place of the glass capsules, porcelain ones may be used and the dried fat and asbestos transferred by a piece of cloth to the extraction apparatus, the little dish being washed with a few drops of ether. A large

number of analyses may be conducted at once, and very concordant results are obtained. H. B.

Determination of Butter in Milk. By H. N. Morse and C. Piggot (*Amer. Chem. J.*, **9**, 108—112).—20 grams of anhydrous copper sulphate is made to cover the bottom of a mortar, and 10 c.c. of the sample carefully run into the powder. In a few minutes, when dry, the contents are ground up with a little sand, and transfered to an extraction tube plugged with cotton-wool, where it is extracted with 10 portions of 10 to 15 c.c. of light petroleum; the fat solutions are concentrated to 10 c.c. or less, and 20 c.c. of decinomal potash solution (in 95 per cent. alcohol) added; after warming for a quarter of an hour, the excess of alkali is estimated by standard acid and phenolphthaleïn. To saponify one gram of butter, 0·230 gram of potassium hydroxide is required. The results agree with those obtained by other methods, and 25 to 30 analyses can be made in the day. H. B.

Colour Tests for Strychnine and other Alkaloïds. By C. L. Bloxam (*Chem. News*, **55**, 155).—Strychnine is dissolved in a drop of dilute nitric acid, and gently heated; to the warm solution a very minute amount of potassium chlorate is added, when an intense scarlet coloration is obtained. Ammonia changes this to brown, and gives a brownish precipitate; the mixture is then evaporated to dryness, when it leaves a dark-green residue, dissolved by a drop of water to a green solution, changed to orange-brown by potash, and again turned green by nitric acid. A table is given showing the colour-changes given by brucine, narcotine, morphine, quinine, cinchonine, and caffeïne on like treatment. The reactions given by various alkaloïds, when boiled with a mixture of potassium chlorate and hydrochloric acid, are also described. A. J. G.

Guaiacum Resin. By H. Hager (*Zeit. anal. Chem.*, **26**, 261).—To distinguish the purified from the natural resin, the latter alone being suitable as a test for ozone, 0·15 gram is dissolved in 5 c.c. of absolute alcohol, and to the solution, filtered in the shade, 10 drops of oil of turpentine are added. If in the course of half an hour the solution turns bluish, the resin has either been purified or has been altered by heat or sunlight. Natural resin gives a solution which remains yellow for several hours. M. J. S.

General and Physical Chemistry.

Index of Refraction of Ice. By G. Meyer (*Ann. Phys. Chem.* [2], **31**, 321—322).—Hitherto the measurements of this index which have been made do not refer to light of any fixed wave-length. The writer therefore communicates some preliminary determinations, both for the ordinary and also the extraordinary ray, for the light from sodium, lithium, and thallium flames. C. S.

Refractive Index and Compressibility of Cyanogen. By J. Chappuis and C. Rivière (*Compt. rend.*, **104**, 1433—1435).—This is a continuation of the authors' work on the refractive power of cyanogen at various pressures. They find that for temperatures between 0° and 30° and pressures between 1 atmos. and 4 atmos., the relation $\frac{n-1}{d}$ = constant, holds good for this gas as for carbonic anhydride and air, and the values obtained by means of this expression differ from those given by the formula $\frac{n_2-1}{(n_2+2)d}$ by quantities which are not greater than the errors of experiment. The numbers calculated by the first formula agree closely with the observed numbers.

C. H. B.

Molecular Refractive Energies of Derivatives of Carbon Bisulphide. By R. Nasini and A. Soala (*Gazzetta*, **17**, 72—78).—Determinations are given of the refractive indices for various rays and the specific molecular refractive energies, according to the formulæ of Landolt and of Lorentz and Lorenz, of allyl sulphide and of various ethereal salts of xanthic acid. The principal results are given in the table below.

	d_4.	$P\frac{\mu_a-1}{d}$.	$P\frac{\mu_a^2-1}{(\mu_a^2+2)d}$.
Allyl sulphide	0·88765	61·74	36·73
Methyl ethyl xanthate	1·11892	65·67	38·15
Diethyl xanthate	1·07400	71·96	42·13
Ethyl dioxythiocarbonate	1·26043	118·28	67·09
Methyl propyl xanthate	1·08409	73·34	42·75
Ethyl propyl xanthate	1·05054	81·39	47·66
Propyl dioxythiocarbonate	1·19661	133·81	74·46

As regards these results, it is noted that in the case of allyl sulphide the found and calculated values are concordant; but in the derivatives of carbon bisulphide the values are not concordant if it is supposed that the atomic refractive energy of the sulphur-atoms is the same as

those in carbon bisulphide. If, however, it is supposed that one of the sulphur-atoms functions as in carbon bisulphide, whilst the other changes its functions and assumes that of a sulphur-atom in the sulphides or mercaptans, then the found and calculated values are concordant.

It would also appear that one of the sulphur-atoms in the dioxythiocarbonates has an atomic refractive energy of 17·42. The difference observed in other cases for the addition of the grouping CH_2 to the molecule is also verified for the homologous ethereal salts of xanthic acid; the isomeric diethyl and methyl propyl xanthates have not, however, identical molecular refractive energies. V. H. V.

Molecular Refractive Energies of the Thiocyanates and Thiocarbimides. By R. Nasini and A. Scala (*Gazzetta*, **17**, 66—72).—In this paper a series of determinations are given of the refractive indices for various rays, and the specific molecular refractive energies of the thiocyanates and their isomerides, the thiocarbimides. The latter values are also compared with those calculated according to Brühl's data, although there remains some uncertainty as to the atomic refraction of sulphur in the thiocyanates, and of nitrogen in the cyanogen compounds generally. The following are the principal results obtained:—

	d_4.	$P\frac{\mu_a-1}{d}$.	$P\frac{\mu_a^2-1}{(\mu_a^2+2)d}$.
Methyl thiocyanate	1·06935	31·75	18·87
Ethyl thiocyanate	1·00715	39·94	23·76
Methyl thiocarbimide	1·06912	35·54	20·77
Ethyl thiocarbimide	0·99525	41·26	25·98
Allyl thiocarbimide	1·00572	50·76	29·71
Phenyl thiocarbimide	1·12891	76·48	43·06
Thiophen	1·05928	41·4	24·13

It will be seen from the above results that the thiocarbimides have a greater refractive (as also dispersive) power than their isomerides; it is also shown that whereas for the first three thiocarbimides the values found for the molecular refractive energies agree with those calculated according to Brühl's data, yet for the phenyl-derivative there is a considerable difference, about 7 per cent. Further, the authors note that their results do not confirm Thomsen's hypothesis that the refractive energy and the heat of combustion are correlative quantities. V. H. V.

Dispersion in Rock-salt. By E. Ketteler (*Ann. Chim. Phys.* [2], **31**, 322—326).—The recent researches of Langley on the spectrum of radiant heat afford sufficient data for the calculation of the constants of Ketteler's dispersion formula,

$$n^2 = -k\lambda^2 + a^2 + D\lambda^2 n/(\lambda^2 - \lambda^2 n).$$

By forming a table of the values of n, the accuracy of the formula is proved for a considerable range of wave-length. k in the case of rock-salt is found to be extremely small = 0·000858. If the substances for which k is known be arranged according to decreasing values of k, the order will be that of the diathermancy of the substances, rock-salt concluding the list.

The physical meaning of the term $-k\lambda^2$ is, therefore, that it represents the absorption of radiant heat, and no dispersion formula wanting this term can be correct. C. S.

Red Fluorescence of Chromiferous Gallium. By L. de Boisbaudran (*Compt. rend.*, **104**, 1584—1585).—The author has previously found (this vol., p. 409) that gallium oxide which contains chromium shows a red fluorescence in a vacuum. The spectrum of this fluorescence shows a very distinct line homologous with the bright lines in the spectrum of the fluorescence of chromiferous alumina and of spinel. The wave-length of this line is λ6897—6898, and it rapidly diminishes in brilliancy as the substance becomes heated by the action of the discharge. The centre of the band in the spectrum of this fluorescence is at λ6619; it is very nebulous at both ends, and extends through λ1080—1180 according to the intensity of the light. C. H. B.

Specific Rotation of Optically Active Substances in very Dilute Solution. By R. Pribram (*Ber.*, **20**, 1840—1850).—Three explanations may be given of the influence of a solvent on the rotatory power of many active substances. 1. The molecules of the substance in solution may be aggregates of simple molecules which undergo dissociation by dilution. 2. The active substance may form hydrates of different, perhaps opposite, rotatory power, the relative quantities of which depend on the amount of water present (Bremer, Abstr., 1885, 622). 3. The solvent may alter the constitution (distance or arrangement of atoms) of the active molecules (Landolt, van t'Hoff). In the first two cases, the rotatory power might be expected to reach a limiting value when the solvent is in sufficient excess; in the last no such limit is probable.

In this third case the author gives a picture of the possible action by imagining four groups to be arranged round an unsymmetrical carbon-atom, at the solid angles of an irregular tetrahedron. A line drawn through them in the order of their magnitude represents the direction of rotation. If the plane containing groups 2 and 3 be supposed to rotate round an axis passing through the carbon-atom, and lying in the plane containing groups 1 and 4 and the carbon-atom, this line will be either a right- or left-handed spiral or a plane curve. The latter position represents an inactive state of the substance.

Recent improvements in the polaristrobometer by Lippich and Landolt have enabled the author to measure accurately the rotation of very dilute solutions of tartaric acid, nicotine, and cane-sugar, with the following results.

Tartaric Acid.—Arndtsen (*Ann. Chim. Phys.* [3], **54**, 403) expresses the rotatory power at 25° by the formula $[\alpha]_D = 1{\cdot}950 + 0{\cdot}1393q$, in

which q, the percentage of water, may vary from 50 to 95. The author gives a number of measurements of rotatory power for solutions containing from 4·7161 down to 0·3471 per cent. of acid. The value of $[\alpha]_D^{20}$ increases from 14·198° to 16·284°. The increase is thus continuous up to the highest dilution.

Nicotine.—The specific rotation (left-handed) of pure nicotine, $[\alpha]_D^{20} = 161·55°$; and Landolt (Abstr., 1878, 1) found that that of the base in solution diminishes rapidly, but irregularly, with increasing dilution. The heat developed when nicotine is mixed with water points to the formation of a hydrate, as does also the following:—When water is added to a solution containing less than 20 per cent. of base, the mixture becomes turbid, and clears only on long standing. When the turbid mixture is heated to 40° it clears rapidly; but again becomes turbid on cooling or on further heating to 50°. Between 50° and 60° the turbidity amounts to milkiness, but still disappears on cooling below 50°. At 70° the nicotine separates as a layer. Furthermore, the rotation of a freshly prepared solution increases with time, and becomes constant only after 48 hours. The author finds the value of $[\alpha]_D^{20}$ to rise from 77·03° for a 4·0289 per cent. solution to 79·319° for a 0·8826 per cent. solution. Thus no limit has been reached.

Cane-sugar.—The rotatory power has been measured by Schmitz (this Journal, 1877, ii, 876) and Tollens (*ibid.*, 875). The latter detected a slight increase when the percentage in solution falls from 70 to 18·86, but a decrease for weaker solutions. Subsequent special experiments by Tollens (Abstr., 1884, 1285) tended to confirm this view. The author's observations show that this decrease is well-marked and tolerably regular. In the table p = percentage of sugar, d density.

p	3·6589	2·0536	1·0131	0·3201	0·2222
d_4^{20}	1·01256	1·00633	1·00224	0·99956	0·99919
$[\alpha]_D^{20}$	66·531°	66·382°	66·002°	65·415°	65·213°

Tollens' formula, $[\alpha]_D = 66·386 + 0·015035p - 0·0003986p^2$, gives results for these weak solutions differing considerably from the author's.

All the results described are at least in harmony with the third hypothesis stated above. CH. B.

Electric Couple with Carbon Elements. By D. TOMMASI and RADIGUET (*Bull. Soc. Chim.*, **47**, 85—88).—The positive element consists of a stick of carbon covered with a layer of lead peroxide and is contained in a canvas bag. The negative element consists of a hollow cylinder of carbon pierced with holes, into this the positive element is thrust, and the whole is placed in a glass cell which is then packed with lumps of gas carbon, and finally a concentrated solution of sodium chloride poured in until the level of the liquid is about half way up the cell. The electromotive force of this couple is from 0·6 to 0·7 volt, and no action occurs in it until the circuit is closed: it,

however, polarises rapidly, and is only suitable for intermittent work, but when thus used it lasts for an almost illimitable time, being in as good condition after two years as when first put up. The chemical action which occurs is an oxidation of the carbon at the negative pole and a reduction of the lead peroxide at the positive pole. A. P.

Nickel and Carbon Elements. By C. v. Neumann (*Dingl. polyt. J.*, **264**, 47).—The author has constructed a battery with nickel and carbon as galvanic elements. The exciting solution is either dilute nitric acid or aqua regia or sulphuric acid, whilst lead dioxide is the depolarising agent. The E.M.F. of this battery is said to be 0·75 volt. D. B.

Galvanic Element. By R. Eisenmann (*Dingl. polyt. J.*, **263**, 540).—The author recommends the use of tungstic acid as an exciting agent for galvanic elements. Its action is similar to that of chromic acid but it has the advantage of being rapidly oxidised after reduction, whilst the addition of a small amount of phosphoric acid suffices to keep the tungstates in solution in the acid liquid. D. B.

Polarisation of Copper by the Extension of the Surface in Contact with a Liquid Conductor. By Krouchkoll (*Compt. rend.*, **104**, 1436—1437).—A spiral of copper immersed in water or in water containing 2 per cent. of sodium sulphate becomes negative at the moment when the surface in contact with the liquid is increased. With a certain degree of polarisation, the phenomenon is reversed, and the copper becomes positive with extension of surface, and with an intermediate degree of polarisation variations in the surface of the metal in contact with the liquid have no effect on the electromotive force. C. H. B.

Conductivity of Amalgams. By C. L. Weber (*Ann. Phys. Chim.* [2], 243—250).—Experiments were made with amalgams of mercury with each of the following metals: tin, bismuth, lead, cadmium. The measurements being made at high temperatures, so as to secure a homogeneous conductor. The resistance of the amalgam contained in a U-tube was found by the method given by Thomson for the determination of small resistances. The electrodes were of iron on account of corrosion. To avoid the influence of thermoelectric effects, the mean of the resistances with the direct and reversed current was taken. An india-rubber tube was attached to the arm of the U-tube, and by suction and compression the amalgam was kept well mixed.

Taking as ordinate the specific resistance and as abscissa the percentage of metal in the amalgam, curves are traced showing the variation of the specific resistance with the composition of the amalgam. All the curves concur in showing that the effect of adding a small quantity of metal to the mercury is to cause a rapid decrease of resistance, and that the conductivity of the amalgam is not the mean conductivity of its constituents. In other respects the amalgams separate into two groups, those of like atomic weight going together. In the tin and cadmium amalgams the resistance, although falling rapidly at

first with increasing percentage of metal, gradually slackens its rate of decrease, and more and more nearly approaches a fixed limit. On the other hand the bismuth and lead amalgams have their resistance decreasing down to a minimum and then rising to a maximum.

The initial character of the curves for these amalgams is therefore different to that of the curves of the alloys of Class 2 which have been investigated by Mathiessen.

In both amalgams and alloys points of maxima and minima occur corresponding to definite chemical combinations. The alloys of mercury with bismuth and lead, however, have this special peculiarity, that they conduct better than either of their constituents.

C. S.

Conductivity of Acids and Salts in Dilute Solutions. By E. Bouty (*Compt. rend.*, **104**, 1611—1614).—The conductivity of dilute solutions of acids and of salts other than normal salts does not follow the simple law which has been found to hold good for normal salts (*Compt. rend.*, **102**, 1097, 1372), a result similar to that obtained in the electrolysis of the same solutions. The resistance at constant temperature is, however, sensibly proportional to a factor $1 + Km^{\frac{1}{3}}$, but the limit and the coefficients in the equation (*loc. cit.*) vary for different substances. Determinations of the conductivity of very dilute solutions of sulphuric, nitric, and hydrochloric acids shows that their molecular resistance varies with the temperature, although within somewhat narrow limits. If the resistance of sulphuric acid is taken as unity at each temperature, the resistances of the other acids in the highest possible degree of dilution are represented by the following numbers :—

	0°.	16°.	32°.
Nitric acid	1·042	1·026	1·017
Hydrochloric acid...	1·053	1·025	1·009

When the resistance of solutions of these acids is compared with that of solutions of their normal salts, it is found that the ratio between the two quantities depends mainly on the temperature, and varies greatly at different temperatures. C. H. B.

Electric Conductivity of Compounds of Potassium and Sulphur in Solution, of Sodium Sulphide and of Boric Acid. By O. Bock (*Ann. Phys. Chem.* [2], **30**, 631—638).—The author has measured the conductivity of mixtures of alkaline hydroxide and alkaline hydrosulphide represented by the formulæ 3KOH + KSH, KOH + KSH = $K_2S(+ H_2O)$, KOH + 3KSH, KSH and Na_2S. The conductivities and temperature coefficients are given in tables for many different concentrations in each case. For these the original paper must be referred to.

The conductivity of KOH, like that of NaOH, is diminished by the addition of hydrogen sulphide. Each mixture of hydroxide and hydrosulphide shows an independent maximum of conductivity for some particular strength of solution, which increases with the amount of hydrosulphide present.

When the solutions are dilute, the conductivities of KOH, K_2S, and

KHS are to each other nearly as $1 : \frac{2}{3} : (\frac{2}{3})^2$. Thus each addition of an electrochemical sulphur molecule, S/2, to one of potassium (or sodium) diminishes the conductivity by one-third. Similarly, the author finds the conductivities of the pentasulphides, K_2S_5 and Na_2S_5, in solution to be about one-third of that of the corresponding sulphide solutions.

The conductivity of various solutions of pure boric acid is also given. This acid is one of the worst known conductors. The trace of sodium present in the commercial acid increases the conductivity threefold. CH. B.

Nobili's Rings and Allied Electrochemical Phenomena. By A. ELSAS (*Ann. Phys. Chem.* [2], **30**, 620—630).—The author believes, in opposition to Voigt, that Nobili's rings are mainly due to currents which traverse the electrolysed liquid nearly parallel to the metal plate. The colours obtained are not in all cases colours of thin plates; but the rings are sometimes deposits of different chemical and physical constitution. In fact, electrochemical decomposition takes place not only at the surfaces of the electrodes, but at every point throughout the liquid traversed by the current. This is proved as follows. Plaster of Paris moistened with copper sulphate solution is poured on a metal plate, and a copper wire plunged into the still soft mass with its end very close to the plate. The plaster is allowed to set firmly, and a current is passed from wire to plate. On removing the cake, four or five coloured rings are seen on its surface, corresponding rings being found on the plate. The plaster also adheres to the metal more or less firmly in different zones, and is also distorted. The central area opposite the wire is green (CuH_2O_2?), and is surrounded by rings successively white, blue, white, red (Cu) and again blue. When the current is long continued, coloured deposits are also found throughout the mass of the gypsum. The colours of the rings are independent of the nature of the metal plate, when the latter does not directly act on the electrolyte.

When the anode wire is of platinum, the electrolyte becomes acid and pure copper is nowhere deposited. When it is of iron, rust-coloured rings are found in the gypsum plate, showing that transference of the ions takes place even in the solid. If the metal plate is made the anode, a blue circle appears round the cathode, surrounded by an intensely blue ring.

When a current is passed between two wires immersed in a plate of gypsum, prepared as above on a plate of glass, circular coloured rings are formed round each wire. The isochromatic lines do not correspond either with the equipotential lines or the lines of equal current-intensity. If in this experiment a metal plate is substituted for the glass, rings also appear on its surface. These appear to coincide with the equipotential lines only at some distance from the wires.

Theoretical views follow as to the distribution of potential in the last case. But the appearances cannot be explained by reference to this alone, as Guébhard imagines. CH. B.

Variations in the Electrical Resistance of Antimony and Cobalt in a Magnetic Field. By G. Faè (*Phil. Mag.* [5], **23**, 540—541).—Rods of antimony when placed in the magnetic field of a Ruhmkorff electromagnet showed an increased electrical resistance, the resistance being greater across the lines of force than along them. Plates of cobalt when so placed showed a diminished resistance when their planes and the current were perpendicular to the lines of force. When placed parallel to them an increase was observed. Further results are promised. H. K. T.

Expansion of Salt Solutions. By W. W. J. Nicol (*Phil. Mag.* [5], **23**, 385—401).—The expansion of the salt solutions is determined in dilatometers heated to constant temperatures by means of the vapour of a liquid boiling under a constant and adjustable pressure maintained by means of a water-pump and a somewhat elaborate pressure regulator. The solutions were made up to molecular strengths by weighing, placed in a vacuum, boiled for ten minutes, cooled, and the composition checked by taking the density in a Sprengel tube. It was found that the results could be expressed by the interpolation formula, $V = 100{,}000 + t'\alpha + t'^2\beta$ where $t' = (t - 20)$. The error being within ± 2 in 100,000. The results showed that the more concentrated the solutions the more nearly did the curves of volume approach a straight line, these being in every case nearer than that of water. Again the value of β being less for water than for any of the solutions, it follows that the volume difference must reach a maximum at some temperature. To find this the volumes of the salt solutions were calculated by interpolation for every 5° between 20° and 100°, as compared with those of water. The following are the maxima found:—

All solutions of	NaCl	55—60°
„	KCl	about 50°
$2NaNO_3100H_2O$	.....	none
$4NaNO_3$	„	„
$6NaNO_3$	„	90—95°
$8NaNO_3$	„	90°
$10NaNO_3$	„	80—85°
$12NaNO_3$	„	80°
KNO_3	„	none
$3KNO_3$	„	80—85°
$5KNO_3$	„	75—80°

With 8 and 10 NaCl and 3, 5, and 7 KCl the volume of the solution at 100° is less than that of water. With NaCl and KCl at 100° the stronger the solution the smaller the volume, whilst with KNO_3 the reverse is the case. In order to compare the results in molecular volumes, the author multiplies by $\frac{1800 + n\text{M.W.}}{\delta}$ (Abstr., 1886, 763). The maxima are now found to be moved up. At high temperatures NaCl and KCl solutions expand less the more concentrated the solutions, whilst with $NaNO_3$ and KNO_3 this is not the case. The author considers this to be due to the effect of temperature on the

solubility of the respective salts, KNO_3 and $NaNO_3$ solutions becoming, so to speak, more dilute at high temperatures. H. K. T.

Tellurium. By Berthelot and C. Fabre (*Compt. rend.*, **104**, 1405—1408).—The different varieties of tellurium were finely powdered and dissolved in bromine and water saturated with bromine, the thermal disturbance being measured. The precipitated varieties were washed and dried in an atmosphere of nitrogen. The following mean numbers were obtained:—

Crystallised tellurium, prepared by volatilisation in hydrogen	+66·66 Cal.
Tellurium precipitated by sulphurous acid	+42·584 „
Tellurium precipitated from alkaline tellurides by the action of air or other oxidising agents	+66·78 „
Tellurium precipitated from hydrogen telluride by oxidising agents	+67·01 „

The tellurium precipitated from hydrogen telluride and alkaline tellurides is identical with the crystalline variety, and the mean heat of solution in bromine and water is +66·776 Cal.

From these results it follows that the conversion of crystallised tellurium into the amorphous variety develops +24·192 Cal., and that tellurium, like sulphur and selenium, exists in two perfectly distinct states. Molten tellurium thrown into cold water and then treated as above gives numbers varying from 44 to 56 Cal., which indicate that it is a mixture of the crystalline and amorphous varieties.

It is worthy of note that the change from amorphous to crystalline tellurium absorbs heat, the corresponding change for selenium develops heat, whilst the similar change in the case of sulphur gives rise to no sensible thermal disturbance at the ordinary temperature, but is positive at a high temperature, and doubtless becomes negative at a low temperature.

It is also of interest that tellurium precipitated in alkaline liquids and from hydrogen telluride, is identical with the crystalline variety, whilst that precipitated by sulphurous acid constitutes a distinct modification. Similar phenomena are observed in the case of sulphur. C. H. B.

Heats of Combustion of Organic Substances. By J. Thomsen (*Ber.*, **20**, 1758—1759).—The author quotes results obtained in the estimation of the heats of combustion of organic substances by Berthelot and Vielle by combustion with oxygen in the calorimetric bomb, and by Stohmann by combustion with potassium chlorate, and points out that the results obtained by the latter are always far lower than those obtained by the former. This he attributes to Stohmann's use of an indirect and an inaccurate method. A. J. G.

Heats of Combustion. By Berthelot and Recoura (*Compt. rend.*, **104**, 1571—1574).—These determinations were made by means of the calorimetric bomb.

Glucose.—Heat of combustion per gram 3·762 Cal.; per gram-mole-

cule +677·2 Cal. This value is sensibly equal to the heat of combustion of lactose, and is identical with half the heat of combustion of saccharose (+677·5 Cal.). These results agree with those previously obtained by Berthelot and Veille. The heat of formation of glucose is +300·8 Cal. The union of carbon in the form of diamond (C_6) with water ($6H_2O$) to form glucose would absorb −113·2 Cal., a result which explains the development of heat during alcoholic fermentation and the reserve energy associated with the carbohydrates which plays such an important part in vital processes.

Quinone.—Heat of combustion per gram 6·102 Cal; per gram-molecule +659·02 Cal. Heat of formation +45·2 Cal. The union of C_6 with $2H_2O$ to form quinone would absorb −92·8 Cal., an absorption relatively greater than that which accompanies the formation of glucose.

Naphthalene.—Heat of combustion per gram 9·6888 Cal.

Benzoic Acid.—Heat of combustion per gram 6·345 Cal.; per gram-molecule +773·1 Cal. at constant volume; 772·8 Cal. at constant pressure. Heat of formation +92·2 Cal. The union of C_6H_6 with CO_2 would absorb −30 Cal.

Salicylic Acid.—Heat of combustion per gram 5·326 Cal.; per gram-molecule +734·99 Cal. at constant volume and constant pressure. This value agrees with that calculated from the heat of combustion of phenol, and the heat of transformation of salicylic acid into phenol and carbonic anhydride. C. H. B.

Heats of Combustion. By Berthelot and Louguinine (*Compt. rend.*, **104**, 1574—1577).—These results were obtained by means of a calorimetric bomb smaller than that used by Berthelot and Recoura (preceding Abstract).

Naphthalene.—Heat of combustion per gram 9·6961. The general mean of this and the previous results is +9·700 Cal. Heat of combustion per gram-molecule +1241·6 Cal. at constant volume; 1242·7 at constant pressure. Heat of formation from its elements −26·7 Cal.

Phenol.—Heat of combustion 7·8105 Cal., which agrees with the previous determination by Berthelot and Vieille.

Benzoic Acid.—Heat of combustion 6·3221 Cal.

Cumic Acid.—Heat of combustion per gram 7·5533 Cal.; per gram-molecule +1239·3 at constant volume, +1237·7 at constant pressure. The excess over the heat of combustion of benzoic acid is + 464·9, or +155 × 3 Cal.

Quinone.—Heat of combustion 6·00613 Cal.

Quinol.—Heat of combustion per gram 6·2295 Cal.; per gram-molecule +685·24 Cal. at constant volume; 684·9 Cal. at constant pressure. Heat of formation +86·1. Heat of formation from hydrogen and quinone +40·9 Cal.

Pyrogallol.—Heat of combustion per gram 5·0262 Cal.; per gram-molecule +633·3 Cal. at constant volume and constant pressure. Heat of formation +137·7 Cal.

$C_6H_6 + O = C_6H_5{\cdot}OH$.....	develops	+36·6 Cal.
$C_6H_5{\cdot}COOH + O = OH{\cdot}C_6H_4{\cdot}COOH$	,,	+37·8 ,,
$C_6H_5{\cdot}OH + O = C_6H_4(OH)_2$	,,	+52·2 ,,
$C_6H_4(OH_2) + O = C_6H_3(OH)_3$	,,	+51·6 ,,

The practical identity of the two last numbers is of considerable interest. The first two changes are not exactly of the same character.

C. H. B.

The Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures. By W. Ramsay and S. Young (*Phil. Mag.* [5], **23**, 435—458).—For perfect gases at constant volume, the pressure varies directly as the absolute temperature, or $p = cT$. This law is at best only approximate, because the actual molecules of gas occupy space, and may be assumed to be incompressible, and because they exercise attraction on one another. If volume be kept constant, however, these two factors are in all probability invariable. Hence it might be expected that at constant volume a gas or a liquid under any conditions of temperature and pressure should exhibit simple relations between temperature and pressure. It has been proved by the authors that this relation is expressible by the formula $p = bT - a$, where b and a are two constants, functions of volume. Amagat from imperfect data has stated a similar relation for gases, but not for liquids. In the paper a full proof of these relations is given from the behaviour of ether and carbonic anhydride. The constants of the former are deduced from measurements by the authors; for the latter Dr. Andrews' data have been employed. Here are three methods of expressing relations between temperature, pressure, and volume; by means of isobars, isotherms, and *isochors* (lines of equal volume). From the above formula it follows that the isochors are straight. They therefore admit of extrapolation without error, and by means of such extrapolation those portions of the isothermals which elude measurement can be mapped. Such isothermals form a sinuous curve, cutting the line representing the observed vapour-pressure, as was predicted by Prof. James Thomson, in three points, and enclosing two areas, one above and the other below the vapour-pressure line. These areas have proved to be equal, thus furnishing a striking confirmation of the correctness of the formula $p = bT - a$, and of the accuracy of the experimental results.

There are three curves obtainable, all representing relations between temperature and pressure: (1) that furnished by the lower apices of the sinuous curves; (2) that furnished by the upper apices; and (3) the ordinary vapour-pressure curve. These three curves cut at the critical point. The critical temperature and pressure are thus given directly. With ether the calculated temperature is 193·83°; that observed was 193·8°. The calculated pressure is 27075 mm. The value of b corresponding with the critical volume is the tangent to the ordinary vapour-pressure curve at the critical temperature. But since no equation is known exhibiting the relations of a and b to the volume (those of Van der Waals, Clausius, and Sarrau being either not convertible into the simpler equation $p = bT - a$, or not repre-

senting facts with sufficient accuracy), the volume corresponding with this value of b can be obtained only by a graphical method. It is for ether, 4·06 c.c. per gram. W. R.

Vapour-tension of Liquid Cyanogen. By J. Chappuis and C. Rivière (*Compt. rend.*, **104**, 1504—1505).—The pressures observed are given in mm., the first number being Bunsen's determination. In order to remove nitrogen, the liquefied cyanogen was made to congeal by its own evaporation in a vacuum, the gas being removed by means of a mercury pump.

Temperature..	−20·7°	0°	5°	10°	15°
Pressure	750	1800	2150	2570	3070

C. H. B.

Vapour-tensions of Saline Solutions. By R. Emden (*Ann. Phys. Chem.* [2], **31**, 145—189).—There are two important questions to be considered, the relation of vapour-tension (1) to temperature, (2) to the amount of salt dissolved. In each case a law of simple proportionality has been enunciated. Thus Babo found that with several salts the vapour-tension was proportional to the tension of the vapour of pure water at the same temperature. The later and more perfect researches of Wüllner, Pauchon, Tammann, and others, do not yield results in accordance with Babo's law. It must be noted, however, that the results of these researches are not concordant, and different conclusions are arrived at with regard to the same salt.

The author's object was to clear the matter up by using a method which had already proved trustworthy. Konovaloff's arrangement (*Ann. Phys. Chem.* [2], **14**, 34) was employed, because it permits the solution to be introduced into the apparatus completely free from air.

To test the exactness of the method, the apparatus was first used to determine the vapour-tension of pure water. The numbers obtained were in close agreement with those of Magnus, and the differences served as some sort of measure of the accuracy of the method.

From the observations by means of Magnus' formula for the vapour-tension—

$$P = a10^{\frac{bt}{c+t}},$$

the constants a, b, c, were calculated. The values were very nearly the same as those Magnus has already given.

Determinations were next made of the vapour-tensions of solutions of varying degrees of concentration of eight different salts (NaCl, KCl, $NaNO_3$, KNO_3, K_2SO_4, $CaCl_2 + 6H_2O$, $ZnSO_4 + 7H_2O$, $CuSO_4 + 5H_2O$).

The author points out the importance of avoiding any small *constant* error of experiment, and alludes to such an error which is to be found in some determinations of vapour-tension by Regnault, who supposes that his thermometers were the cause of it.

In the researches of Wüllner and Tammann, cathetometers were

used. The error might be caused by the barometer-tube being inclined to the plane glass face of the water tank, or by the condensation of the vapour on the sides of the tube.

A formula similar to that given by Magnus may be supposed to hold for a salt solution, so that—

$$p = a'10^{\frac{b't}{c'+t}}.$$

It easily follows analytically that, if Babo's law holds, $b = b'$ and $c = c'$. The observations may then be used to determine the value of a', and a table of the values of p may be constructed. The differences between the values of p as observed and as given by the formula were found to be within the limits of experimental error already determined. It was therefore concluded that for a range of temperature from 20° up to 95°, Babo's law was true.

Wüllner asserts that the alteration of vapour-tension is proportional to the amount of salt dissolved. This law, however, is not in accordance with the results of experiments of Pauchon, Tammann, and others. The present observations prove that Wüllner's law is incorrect. In conclusion, the formula for p is extended to the calculation of the boiling points of the solutions. C. S.

Apparatus for Vapour-density Determinations. By D. S. Macnair (*Chem. News*, **55**, 289).—The apparatus is a simplification of Hofman's, and consists of a syphon barometer-tube, filled with mercury, and suspended in an outer tube, in which some liquid of constant boiling point is heated, so as to surround the syphon tube by its vapour. A weighed quantity of the substance is passed round the bend of the syphon, and rises through the mercury to the slightly widened upper end of the tube, where its vapour soon depresses the mercury. Observations of the volume occupied, the temperature, and the barometer, complete the necessary data for calculating the vapour-density. A determination of the density of toluene vapour gave 46·3, the theoretical number being 46·0. R. R.

Hydrates of Barium and Strontium Hydroxides. By W. Müller-Erzbach (*Ber.*, **20**, 1628).—A repetition of the experiments on the vapour-tension of hydrated barium and strontium hydroxides at temperatures between 15° and 70° has confirmed the results previously obtained (comp. this vol., p. 208), inasmuch as barium hydroxide was always found combined with one, two, seven, and eight molecules, and strontium hydroxide with one, seven, and eight molecules of water. At 15° the vapour-tension of $BaH_2O_2 + 8H_2O$ amounted to 11·4 mm.; of $BaH_2O_2 + 3$ to $7H_2O$ to 2·46 mm.; of $BaH_2O_2 + 2H_2O$ to 1·3 mm. (at first 1·5 mm.); of $BaH_2O_2 + H_2O$ to *nil;* of $SrH_2O_2 + 8H_2O$ to 9·4 mm.; of $SrH_2O_2 + 2$ to $7H_2O$ to 3·2 mm., and of $SrH_2O_2 + H_2O$ to *nil.* This difference between barium hydroxide and strontium hydroxide is not altered when the respective hydrates containing 1 mol. of H_2O are placed in a moist atmosphere until each has taken up 2 mols. of H_2O, since the hydrated strontium hydroxide lost the absorbed water at a constant vapour-

tension, whilst the barium compound gave off water at a tension of 2·5 mm. until it acquired the composition $BaH_2O_2 + 2H_2O$, and lost the second mol. of H_2O at a tension of 1·3 mm. W. P. W.

Hydrates of Barium Chloride. By H. Lescœur (*Compt. rend.*, **104**, 1511—1513).—The following are the vapour-tensions at 100°:—

Saturated solution.	$BaCl_2 + 2H_2O$.	$BaCl_2 + 1·9H_2O$.
About 664 mm.	620 mm.	626 mm.
$BaCl_2 + 1·2H_2O$.	$BaCl_2 + 0·94H_2O$.	$BaCl_2 + 0·18H_2O$.
615 mm.	272 mm.	270 mm.

These results indicate the existence of a dihydrate and monohydrate. The latter is not formed at 100°, since dehydration becomes complete at this temperature, but is readily obtained by heating the dihydrate at 60—65°. In presence of moist air the dihydrate takes up some water, the vapour-tensions at +10 being—

$BaCl_2 + 2H_2O$.	$BaCl_2 + 2·25H_2O$.	$BaCl_2 + 2·40H_2O$.	$BaCl_2 + 2·61H_2O$.
2·7 mm.	7·5 mm.	7·5 mm.	7·4 mm.

These results indicate the existence of a higher hydrate, which, however, has not yet been isolated, but the fact that the addition of barium chloride to a supersaturated solution of calcium chloride determines the separation of the hexahydrate, $CaCl_2 + 6H_2O$, seems to point to the existence of a hexahydrate of barium chloride.

C. H. B.

Amount of Water of Crystallisation contained in some Salts. By C. R. Schulze (*Ann. Phys. Chem.* [2], **31**, 204—233).—The method of investigating the constitution of a salt by measuring the vapour-tension by the barometric method seems free from objection, but there are very considerable practical difficulties in carrying it out. Müller-Erzbach has proposed a somewhat easier plan, namely, to measure the relative vapour-tension. The present research was directed to test the accuracy of Müller-Erzbach's method.

Twelve tubes of three different sizes with spherical bulbs blown at their ends were used. Some were filled with zinc sulphate in the shape of powder, and others with small crystals of zinc sulphate, whilst three were filled with water. By determining the loss of weight from day to day the relative tension was obtained. The tabulated results prove that the quantity of water evaporated is not proportional to the cross section of the tubes. The tubes containing the crystals give much higher values of the tensions than those containing the powder. It is inferred that Müller-Erzbach's method is untrustworthy.

Müller-Erzbach supposed that the relative tension increased with the temperature, but the author adduces observations made by Wiedemann to show that it is very nearly constant. This last result is of importance, because it enables us to deduce the vapour-tension for a salt from the corresponding tension of water-vapour.

Müller-Erzbach has deduced from his observations the existence of a sulphate of zinc having the formula $ZnSO_4 + 5H_2O$, but Schulze proves that Müller-Erzbach is hardly consistent in his mode of interpretation of the results of his experiments.

Wiedemann had discovered a modification of magnesium sulphate with 6 mols. H_2O produced at a temperature of 93°, which differs from the crystals produced between 50° and 60° by having a greater density. The author by measurements with the specific gravity bottle confirms the existence of this modification. C. S.

Decomposition of Acetates by Water. By G. Foussereau (*Compt. rend.*, **104**, 1265—1267).—When aqueous solutions of zinc, copper, and lead acetates are allowed to remain at the ordinary temperature the resistance gradually increases, and this indicates a partial dissociation of the salt, since the resistance of free acetic acid is higher than that of its salts. The resistance increases with a rise of temperature and diminishes with a fall of temperature, tending towards a definite limit in each case. The dissociation is greatest in the case of cupric acetate, and somewhat less in the case of zinc acetate. Lead acetate shows similar changes in a very much lower degree.

In concentrated solutions the dissociation is very slightly marked even at high temperatures, and when the solution is diluted the resistance at first increases with the dilution, attains a maximum, and then decreases when the solutions become very dilute. The phenomena consequent on dilution are therefore different from those observed in the case of chlorides. C. H. B.

Velocity of Saponification. Part III. By L. T. Reicher (*Annalen*, **238**, 276—286).—Urech (Abstr., 1885, 480) has recently stated that when two substances A and B act on each other, the rate of saponification is influenced to a different extent by an excess of A than by an excess of B. The author has repeated his experiments on the saponification of ethyl acetate, and proves that the rate of saponification remains the same whether excess of sodium hydroxide or excess of ethyl acetate is doubled. W. C. W.

Action of Heat on Potassic Chlorate and Perchlorate. By E. J. Mills (*Phil. Mag.* [5], **23**, 375—378).—The author investigates as instances of cumulative resolution the results obtained by Teed, and by Frankland and Dingwall (Proc., 1885, 105; 1886, 141; 1887, 24 and 25) on the decomposition by heat of potassic chlorate and perchlorate.

Representing the reaction by the equation $2nKClO_3 - (n-2)O_2 = (n+1)KClO_4 + (n-1)KCl$, and taking r = specific measure of the change $= \frac{\text{p. c. KCl in } KClO_3}{\text{p. c. O in } KClO_3}$, then $r \times \frac{O_2}{KCl} = \frac{n-1}{n-2}$.

The value of n calculated from the results of the above experimenters is always rational, and approximates to r, a result which reduces the change to a mass action. For potassic perchlorate the equation $(n+1)KClO_4 - (2n-1)O_2 = 2KClO_3 + (n-1)KCl$ is

taken, and the values for n calculated as before. From these values the ratio $\frac{KCl}{KClO_3} = p$ is calculated from the equation $p \times \frac{KClO_3}{KCl} = \frac{n-1}{2}$, and the values compared with those obtained from analytical data. They agree well in two cases out of three; in the third case the value for n was large.

If the weight of chloride = that of oxygen, then $r = 1$. If the values for n be now calculated from the two equations they are found to be reciprocal, hence the perchlorate reaction is the exact inverse of the chlorate reaction. H. K. T.

Influence of Temperature on the Coefficient of Speed of Inversion of Cane-sugar by Hydrochloric Acid. By F. Urech (*Ber.*, **20**, 1836—1840).—The author shows that this influence as deduced from his experiments (Abstr., 1883, 174; 1885, 41) is not expressed by the formula arrived at by Spohr (Abstr., 1886, 502), $K = a^{t+b}$, in which t is reckoned from 0° and b is arbitrary. In the series of experiments quoted, the calculated value of a is nearly constant throughout, whilst b increases rapidly both with the temperature and with the concentration of the acid. On the other hand, Van t'Hoff's formula, $\log K = -\frac{A}{T} + BT + C$, expresses the results for any particular strength of acid fairly well when the constants A, B, and C are determined from observations at wide intervals of temperature. These constants, however, vary for acids of different strengths, and even for any particular concentration their values depend on the temperatures for which they are calculated. Ch. B.

The Spheroidal State. By Gossart (*Compt. rend.*, **104**, 1270—1272).—The author has repeated Luvini's experiments (*Il Nuovo Cimento*, 17) with an apparatus so modified that the volume of the liquid, the temperature, and the pressure remained constant, and the two latter can be accurately measured.

Below 33° the temperature of the spheroid is higher than the boiling point of the liquid at the particular pressure. From 33° to 50° the two numbers are practically identical, the differences being sometimes positive and sometimes negative. From 50° up to 90° the temperature of the spheroid is always lower than the boiling point of the liquid under the existing pressure. At low temperatures the differences increase somewhat regularly, but at high temperatures the variations are comparatively irregular.

Under a pressure of 0·5 mm. a drop of water weighing 2 grams was completely frozen whilst in the spheroidal state, and was kept in this condition for 15 minutes, notwithstanding the fact that the dish on which it was supported was heated by means of a blowpipe.

C. H. B.

Decrease of the Compressibility of Ammonium Chloride Solutions with Increase of Temperature. By F. Braun (*Ann. Phys. Chem.* [2], **31**, 331—335).—The measurements were made with

an Oersted's piezometer, the solution being contained in a dilatometer. Care was taken to expel as far as possible all air from the solution, and to diminish errors arising from this source, large pressures were employed. A rise of temperature of about 18° produced a diminution of about 3 per cent. in the compressibility, whether the liquid surrounding the dilatometer was water or ammonium chloride solution. This alteration cannot be ascribed to errors of experiment, and it is shown that the thermal effect of compression would not produce so large a change, although it would affect the absolute value of the coefficient. The comparison of the author's results with those obtained in the recent research of Schumann shows that the coefficients found are smaller, but that in each case the temperature coefficient of compressibility has the same sign. C. S.

Lecture Experiments. By A. Mermet (*Bull. Soc. Chim.*, **47**, 306—310).—Silicon hydride may be conveniently prepared in small quantity for a lecture experiment by placing a piece of magnesium ribbon in a glass tube about 6 cm. long, and closed at the lower end, and heating in a Bunsen flame; after cooling, a few drops of hydrochloric acid are poured on the small globule of the silicon and aluminium compound formed, when an evolution of silicon hydride takes place, the bubbles burning in the air with decrepitation, and leaving a cloud of silica. If it be wished to prepare the gas in larger quantity it may be done by twisting one end of a stout wire round the rim of a steel thimble, and fixing the other end in a suitable support; a mixture of silica or sand and magnesium powder is then heated in this small improvised crucible, and the experiment conducted as before.

Potassium ferrate may be prepared in quantities sufficient to demonstrate its properties by adding excess of a concentrated solution of potash to 0·5 c.c. of a strong solution of ferric chloride, then a good pinch of bleaching powder, and finally a fragment of potassium hydroxide of the size of a pea, the solution is next filtered through asbestos, and the reddish-violet solution obtained contains sufficient potassium ferrate with which to demonstrate all the characteristic reactions of that salt. The author further calls attention to a violent explosion which took place when preparing hypochlorous anhydride, with use of a mixture containing liquid methyl chloride to condense the gas. A. P.

Inorganic Chemistry.

Methods for obtaining Sulphurous Anhydride and Oxygen by the Use of a Kipp's Apparatus. By G. Neumann (*Ber.*, **20**, 1584—1585).—Sulphurous anhydride can be generated in a Kipp's apparatus by the action of ordinary concentrated sulphuric acid on cubes prepared by Winkler's method (this vol., p. 442) from a mixture of 3 parts of calcium sulphite and 1 part of gypsum. Economy in

the use of the cubes is effected, if only the number required for the generation of the amount of gas needed are wetted with the acid at the commencement of the operation.

To prepare oxygen in a Kipp's apparatus, cubes consisting of a mixture of 2 parts of barium dioxide, 1 part of manganese dioxide, and 1 part of gypsum are used with hydrochloric acid (sp. gr. = 1·12) diluted with an equal volume of water. The oxygen evolved contains traces of chlorine, and must therefore be washed with an alkali.

It is not advisable to replace the gypsum in the cubes by starch or other similar cementing material. W. P. W.

Vapour-density of Tellurium Tetrachloride: Valency of Tellurium. By A. Michaelis (*Ber.*, **20**, 1780—1784).—Tellurium tetrachloride boils constantly at 380°. The vapour-density was determined in V. Meyer's apparatus at the temperature of boiling sulphur (448°) and of boiling phosphoric sulphide (530°). The density found in each case was that required by the formula $TeCl_4$, so that the vapour of tellurium sulphide does not suffer much dissociation even at 150° above its boiling point. From this result it follows that tellurium is at least tetravalent. The result is the more important, seeing that sulphur tetrachloride is only stable in the liquid state at −21°, and that selenium tetrachloride gives at 218° a vapour-density showing dissociation into selenium chloride and free chlorine ($Se_2Cl_2 + 3Cl_2$). The densities determined for tellurium tetrachloride were—

At 448°.		At 530°.		Calculated for $TeCl_4$.
9·028	9·224	8·859	8·468	9·32

A. J. G.

Nitrogen Fluoride. By H. N. Warren (*Chem. News*, **55**, 289).—Oily-looking drops found on the negative pole on electrolysing a solution of ammonium fluoride were supposed to be nitrogen fluoride. When connected with the positive electrode (a thin gold wire) these drops exploded with great violence, and the same thing occurred when they were brought into contact with glass, silica, or organic matter. No analyses seem to have been attempted.

R. R.

Regeneration of Acid Residues in the Manufacture of Gun-cotton. By E. Allary (*Bull. Soc. Chim.*, **47**, 102—103).—The acid residues, which have a mean density of about 58° Baumé, are filtered through sand to remove a small amount of nitrocellulose, and then distilled. 100 kilos. yield 10 077 kilos. of nitric acid of 50° Baumé, 6·279 kilos. of nitric acid of 10° Baumé, and 82·302 kilos. of colourless sulphuric acid of 62° Baumé, the loss amounting to 1·342 kilos.

These acid residues may also very economically replace sulphuric acid in the manufacture of nitric acid from crude commercial sodium nitrate, nitric acid of 48·45° Baumé being obtained at the first distillation. There appears to be no danger of any explosive action caused by the presence of nitrocellulose dissolved in the acids.

A. P.

Influence of Pressure and Temperature on the Action of Potassium Chloride on Crude Methylamine Carbonate. By J. A. Muller (*Bull. Soc. Chim.*, **47**, 379—382).—The crude amines employed contained 1 per cent. of ammonia, 30 per cent. of methylamine, 50 per cent. of dimethylamine, 2 per cent. of trimethylamine, and about 17 per cent. of higher amines containing a considerable amount of amylamine. The dilute carbonic anhydride employed was obtained from a limekiln, and contained 25 per cent. of carbonic anhydride. The potassium chloride employed was Stassfurt salt, containing 97·3 per cent. of potassium chloride. 2·14 mols. of the methylamine carbonate were taken to every 2 mols. of potassium chloride. Under these conditions it was found that the conversion of the potassium chloride into hydrogen potassium carbonate took place most satisfactorily, either under ordinary pressure at a temperature of 0°, or at the ordinary temperature under a pressure of about 3 atmospheres.

A. P.

Artificial Production of Trona or Urao. By P. de Mondésir (*Compt. rend.*, **104**, 1505—1508).—A mixture of crystallised sodium carbonate 27 parts and sodium hydrogen carbonate 8 parts, is added gradually to a boiling solution of 28 parts of sodium chloride and 28 parts of crystallised sodium carbonate in 100 parts of water. The liquid is boiled until solution is complete, water being added to replace that lost by evaporation, and is then allowed to cool slowly, care being taken that the temperature does not fall below 20°. The carbonate, $3Na_2O,4CO_2,5H_2O$, is deposited in long, white needles, which are usually matted together. This compound is stable in saturated solutions of sodium chloride, in which it is only slightly soluble, and in presence of which it loses carbonic anhydride very slowly, even when boiled. If a mixture of the 3 : 4 carbonate and sodium chloride is treated with water, part of the carbonate dissolves unchanged, and part is decomposed into the normal carbonate and the hydrogen carbonate. The 3 : 4 carbonate can, however, be separated from the chloride by dissolving the mixture in hot water, and allowing to cool, when the unaltered carbonate separates almost immediately, and is purified by washing with cold water. With the proportions given above, the carbonate is obtained practically free from chloride.

This artificial carbonate is identical in composition, crystalline form, &c., with natural trona or urao. C. H. B.

Silver Suboxide. By G. H. Bailey (*Chem. News*, **55**, 263).—The author thinks that Pfordten's results (this vol., p. 699) fail to establish the existence of silver suboxide, as they do not include the preparation of any definite salt of the base, but merely a partial analysis of a black powder of problematic constitution. R. R.

Solubility of Calcium and Magnesium Chlorides in Water at 0°. By R. Engel (*Bull. Soc. Chim.*, **47**, 318—320).—The results given by various authors who have examined the solubility of these salts are very discrepant, the author finds, as the result of very careful experiment, that 100 parts of water at 0° dissolve 60·3 parts of calcium chloride, the solution having a sp. gr. of 1·367. 100 parts of water

at 0° dissolve 52·2 parts of anhydrous magnesium chloride. The saturated solution has a sp. gr. of 1·3619 at 15°. A. P.

Solubility of Lead Chloride in Solutions of Mercuric Chloride. By J. Formánek (*Chem. Centr.*, 1887, 270—271).—Results are given to show that the solubility of lead chloride in a solution of mercuric chloride is greater than in water, although the increase in solubility seems not to be due to the formation of a double salt. V. H. V.

Ammonium Copper Iodides. By A. Saglier (*Compt. rend.*, **104**, 1440—1442).—100 grams of ammonium iodide is dissolved in 10 times its weight of water, and mixed with 10 to 15 grams of copper hydroxide, which partially dissolves in the cold and is completely soluble on heating. The liquid is then boiled with a large excess of copper until it becomes colourless, concentrated, and allowed to cool slowly, when it deposits long, white needles, of the composition $Cu_2I_2,2NH_4I + H_2O$. These crystals can only be preserved in the mother-liquor, and even under these conditions become brown after some time. In air they lose ammonia and ammonium iodide, and when heated, yield black cuprous iodide. They are decomposed by water with separation of cuprous iodide, and also by alcohol. When the original mother-liquor is exposed to the air it deposits black crystals of the composition $Cu_2I_2,2NH_4I,2NH_3 + 4H_2O$.

If the solution of cupric oxide in ammonium iodide, obtained as above, is allowed to cool without being boiled with metallic copper, it deposits black needles of the composition $CuI_2,2NH_4I,2NH_3 + 2H_2O$, which may be preserved in the mother-liquor, but alter when exposed to air. They are insoluble in water and ethyl alcohol, and dissolve with difficulty in ammonia. When the ammoniacal solution cools it deposits blue crystals of the composition $CuI_2,4NH_3 + H_2O$, which are decomposed by heat, the final product being cuprous iodide.

If cupric hydroxide is dissolved in ammonium di-iodide, analogous compounds containing the di-iodide are obtained. A solution of ammonium iodide is mixed with an equivalent quantity of iodine and treated as above, the solutions being somewhat more dilute. The product consists of violet-black needles of the composition $CuI_2,2NH_4I_2,2NH_3 + 6H_2O$, which are red by transmitted light. They are more stable than the corresponding compound containing ammonium moniodide, but alter when exposed to air, and are even decomposed by water. They dissolve with difficulty in dilute ammonia.

The ammonium cupric iodides yield black cupric oxide when treated with potassium hydroxide; the cuprous iodides yield cuprous oxide. C. H. B.

Solubility of Copper Sulphate. By A. Étard (*Compt. rend.*, **104**, 1614—1616).—The curve which represents the percentage composition of the saturated solution of a salt at different temperatures is usually a straight line. In the case of copper sulphate the direction of the line changes at three points.

Starting with the ordinary hydrate, $CuSO_4 + 5H_2O$, the quantity

of anhydrous copper sulphate in 100 parts of the solution between $-2°$ and $+55°$ is given by the equation $y = 11{\cdot}6 + 0{\cdot}2614t$, and between $+55°$ and $105°$ by the equation $y = 26{\cdot}5 + 0{\cdot}3700t$. Between these limits no formation of a definite hydrate can be detected, but there are perturbations in the conditions of equilibrium, and small quantities of a basic salt, $3CuSO_4,4CuO + 12H_2O$, are deposited. Between 105° and 190°, however, the percentage quantity of anhydrous salt is given by the expression $y = 45{\cdot}0 - 0{\cdot}0293t$, and the solubility diminishes with a rise of temperature. These last conditions correspond with the formation of a trihydrate, $CuSO_4,3H_2O$.

This hydrate is obtained by heating at 108—110° a flask containing a boiling saturated solution of copper sulphate. After about 48 hours' continuous evaporation the larger crystals were separated and preserved in sealed tubes. The crystals of the trihydrate are paler in colour than those of the pentahydrate, and break up in moist air, absorbing $2H_2O$. They have two optical axes, and seem to be rhombic octahedra. The same hydrate can be obtained in the amorphous condition by the careful dehydration of the pentahydrate. C. H. B.

Schweizer's Reagent and "Eau Celeste." By H. Baubigny (*Compt. rend.*, **104**, 1616—1618).—"Eau celeste" is obtained by dissolving copper salts in ammonia, and contains salts of the type $CuSO_4,4NH_3 + H_2O$. Schweizer's reagent is prepared by treating cupric hydroxide with ammonia, and contains the base $CuO,4NH_3 + 4H_2O$, isolated by Malaguti and Sarzeau. Both solutions deposit cupric hydroxide when largely diluted. "Eau celeste" contains salts of the base which exists in the free state in Schweizer's reagent. It follows that solutions of basic cupric salts should behave as mixtures of "eau celeste" and Schweizer's reagent, and this is found to be the case. Such solutions dissolve cellulose more readily the more basic the salt. Conversely, the addition of an ammonium salt to Schweizer's reagent partially converts it into "eau celeste," and if the former has previously been saturated with cellulose, the cellulose is precipitated as the ammonium salt is added. This change is produced by ammonium carbonate and by carbonic anhydride, and it follows, therefore, that when Schweizer's reagent is exposed to the air it will form cuprammonium carbonate, and will eventually be converted into "eau celeste."

The old method of preparing Schweizer's reagent by dissolving copper in ammonia in presence of air is defective, since it does not avoid the presence of carbonic anhydride, and hence gives a product with diminished solvent powers. Potassium sulphate and sodium chloride are not decomposed by ammonia nor by the cuprammonium base, and therefore they do not affect the properties of Schweizer's reagent. The addition of potassium or sodium hydroxide to "eau celeste" produces a liquid which is capable of dissolving cellulose.

The best method of preparing Schweizer's reagent is to precipitate a solution of copper sulphate with the calculated quantity of soda and dissolve the hydroxide in ammonia.

There can be little doubt that the Schweizer's reagent distributed

over vines as a preventative of mildew will be rapidly transformed into "eau celeste," which is the actual preservative. The more easily prepared "eau celeste" can therefore be used for this purpose instead of the Schweizer's reagent. C. H. B.

Stability of Corrosive Sublimate Solutions. By V. Meyer (*Ber.*, **20**, 1725—1729).—Anreger has recently stated that solutions of mercuric chloride in ordinary (not distilled) water can be rendered sufficiently permanent for antiseptic purposes by the addition of sodium chloride in weight equal to that of the mercuric chloride, the precipitation of mercuric oxychloride being thus prevented. The author's experiments fail to confirm this statement even with a large excess of sodium chloride; precipitates being still formed in solutions made with ordinary water. A. J. G.

Behaviour of Mercuric Chloride with Hydrogen Ammonium Carbonate. By K. Thümmel (*Arch. Pharm.* [3], **25**, 245—249).—Hydrogen sodium carbonate containing not more than 0·1 per cent. of hydrogen ammonium carbonate in solution, gives a white turbidity with mercuric chloride; if more is present, a white, flocculent precipitate is produced which quickly becomes yellow, and if the mercury salt is not added in excess, almost the whole of it is found in the precipitate. This precipitate was found to have approximately the composition $3HgO,HgCl_2 + NH_2HgCl$.

A similar precipitate obtained with pure ammonium carbonate had the formula $HgO,HgCl_2 + 2NH_2HgCl$. The yellow residue obtained on boiling *hydr. præc. alb* in water, and found by Kane (*Ann. Phys. Chem.*, **48**, 182) to be HgO,NH_2HgCl, was found by the author to contain $(HgO,NH_2HgCl)_6 + HgCl_2$. J. T.

Action of Carbonic Anhydride on Ultramarine. By E. Büchner (*Chem. Zeit.*, **11**, 314).—Carbonic anhydride when passed into water containing ultramarine in suspension, causes an evolution of hydrogen sulphide. If the passage of the carbonic anhydride is continued until the evolution of hydrogen sulphide ceases, and during the passage of the gas the water is frequently changed by decantation, after subsidence of the ultramarine, a considerable amount of soda is found in solution. The author explains the reaction by supposing that ultramarine contains sodium sulphide, and that this sulphide is decomposed by carbonic anhydride, although nitroprusside of sodium fails to give any indication of the presence of an alkaline sulphide in the ultramarine. The reaction takes place also when carbonic anhydride is passed over dry ultramarine in a finely divided state. Ultramarine when acted on by carbonic anhydride whilst suspended in water, loses its fine blue tone, the product when dried being of a dull-red colour. J. P. L.

Manganese Sulphate. By B. Claassen (*Arch. Pharm.* [3], **25**, 310).—To obtain crystals of manganese sulphate of definite composition is usually difficult; those obtained below 6° contain 7 mols. H_2O,

between 7° and 20° 5 mols. H_2O, and between 20° and 30° 4 mols. H_2O; frequently also the crystallisation only takes place after a long time. The author overcomes the difficulty by treating a concentrated solution of sulphate with 95 per cent. alcohol, when almost the whole of the sulphate separates out as a syrupy liquid, which after a short time begins to form crystals. If, at this point, the liquid and alcohol be repeatedly and strongly shaken, a crystalline meal results, but if allowed to remain at rest, well-formed, reddish-white, prismatic crystals are formed, identical with those obtained between 7° and 20° before-mentioned, and having the formula $MnSO_4 + 5H_2O$.

J. T.

Action of Selenious Acid on Manganese Dioxide. By P. Laugier (*Compt. rend.*, **104**, 1508—1511).—Powdered native manganese dioxide is not readily attacked by a saturated solution of selenious acid even in sealed tubes, but precipitated hydrated manganese dioxide is readily dissolved with development of heat. The solution is brown, and seems to contain a selenite of manganese dioxide, but, like the solution of the dioxide in hydrochloric acid, it readily decomposes, manganese selenate remaining in solution, whilst an orange compound is precipitated. No oxygen is evolved. The precipitate contains manganese sesquioxide and selenious anhydride, but usually retains unaltered manganese dioxide.

An orange-yellow compound, $Mn_2O_3,4SeO_2$, is obtained by heating hydrated manganese dioxide, $MnO_2 + 4H_2O$ (1 mol.) and selenious anhydride (6 mols.) in sealed tubes with water at 140° for about eight hours. It is insoluble in water, and is not attacked by concentrated sulphuric or nitric acid in the cold. If these acids are diluted with three or four times their bulk of water, they have no action on the compound even when boiled. The compound is dissolved by selenious acid with subsequent precipitation of selenium, is attacked by cold hydrochloric acid with evolution of chlorine, and is dissolved by alkalis with formation of a selenite and manganese sesquioxide. It does not lose water at 200°, but at 600° selenious anhydride is volatilised, and a rose-coloured residue of manganous selenate is left.

If the preceding compound is heated with water in sealed tubes at 140° for about four hours, small, green prisms of the compound $Mn_2O_3,2SeO_2$ are obtained. This substance does not lose selenious anhydride at 600°, but in other respects it behaves like the preceding compound. It is obtained directly by heating a concentrated solution of selenious anhydride (2 mols.) with hydrated manganese dioxide (1 mol.).

If the second compound is left in contact with a solution of selenious acid for about a month, it is converted into a well-crystallised, red compound with properties similar to those of the original substance. It has the composition $Mn_2O_3,3SeO_2,5H_2O$, loses water at 200°, and selenious anhydride at 600°.

C. H. B.

Cobaltammonium Compounds. By S. M. Jörgensen (*J. pr. Chem.* [2], **35**, 417—448).—The following formulæ are assigned to the luteocobalt salts described (compare *J. pr. Chem.* [2], **23**, 229, and

Abstr., 1884, 1093) :—$(Co_2,12NH_3)6NO_3$, the reactions of the solution, with a number of reagents are also described; $(Co_2,12NH_3)2NO_3,2SO_4$, corresponding with a chromium compound; $(Co_2,12NH_3)2NO_3,2PtCl_6 + 2H_2O$, also corresponds with a chromium salt; it is not decomposed by water; $(Co_2,12NH_3)Cl_6$ is anhydrous and very stable, not being changed by strong hydrochloric acid at 100°, whilst the corresponding chromium salt changes into the purpureochloride even in the cold; $(Co_2,12NH_3),3PtCl_6 + 6H_2O$; this salt was first examined with correct results by Gibbs and Genth; they however claim to have obtained also $(Co_2,12NH_3)3PtCl_6 + 21H_2O$, this was probably the salt $(Co_212NH_3)Cl_2,2PtCl_6 + H_2O$; $(Co_212NH_3)Cl_4,PtCl_6 + 2H_2O$ is also described; these three platinum double chlorides easily undergo change, the one being converted into the other. The crystals of the second salt contain many cavities full of liquid. $(Co_212NH_3)Cl_4,2HgCl_3$ and $(Co_212NH_3)6HgCl_3 + 2H_2O$ are described, but it is believed that the salt described by Carstanjen with $4HgCl_2$ does not exist. $(Co_2,12NH_3)Br_6$; $(Co_2,12NH_3)Br_2,2SO_4$; $(Co_2,12NH_3)Br_2,2PtBr_6 + 2H_2O$; $(Co_2,12NH_3)I_6$ must be prepared from the hydrate; $(Co_2,12NH_3)3SO_4,5H_2O$, this salt contains $5H_2O$, as Gibbs and Genth showed, and not $4H_2O$, as described by Fremy and Genth; $(Co_212NH_3)2SO_4,2AuCl_4$; $(Co_2,12NH_3)2SO_4,2AuBr_4$; $(Co_2,12NH_3)2PO_4 + 8H_2O$ can be obtained more simply than originally described by Braun; $(Co_2,12NH_3)3PO_4H + 4H_2O$. These salts are described in detail in the original.

The pyrophosphate has been examined by Braun, Gibbs, Vortmann, and Porumbaru; when a cold solution of luteocobalt chloride is precipitated with sodium pyrophosphate, the salt $(Co_212NH_3)2P_2O_7Na + 23H_2O$ is formed; when washed with hot water it is converted into $(Co_212NH_3)_2,3P_2O_7 + 20H_2O$; if, however, the component salts are mixed hot, then a third salt,

$$(Co_212NH_3)3P_2O_7,(Co_212NH_3)_22P_2O_7Na,39H_2O,$$

is formed, but under no such conditions is an acid salt ever obtained, as has been reported by other investigators; the acid pyrophosphate is formed by treating the above with dilute acetic acid; its composition is $(Co_212NH_3)2P_2O_7H$; a corresponding acid, roseocobalt pyrophosphate, $(Co_2,10NH_3,2H_2O)2P_2O_7H$, is also described; some further details are also given respecting the salt $(Co_2,12NH_3)Co_2Cy_{12}$.

H. B.

Chromiodates. By A. Berg (*Compt. rend.*, **104**, 1514—1517).—*Chromiodic acid*, $IO_2{\cdot}O{\cdot}CrO_2{\cdot}OH + 2H_2O$, is obtained by dissolving chromic anhydride (1 mol.) and iodic acid (1 mol.) in a small quantity of water, and evaporating over sulphuric acid. It forms small, ruby-red, deliquescent, rhombic crystals, which melt when heated, then lose water, and finally give off oxygen. Chromiodic acid oxidises alcohol, but with less energy than chromic acid.

Potassium chromiodate, $IO_2{\cdot}O{\cdot}CrO_2{\cdot}OK$, is obtained by concentrating a solution of potassium dichromate (1 mol.) and iodic acid (2 mols.) containing a slight excess of chromic acid, or by dissolving potassium iodate in an excess of chromic acid. It forms brilliant red, anhydrous, crystalline crusts, and sometimes isolated crystals; sp. gr. = 3·66.

In presence of a large excess of chromic acid it separates in orange-yellow plates.

The ammonium salt is obtained in a similar manner, and forms red, rhombic crystals, which are somewhat more soluble than the potassium salt; sp. gr. = 3·50. A hydrated salt containing 1 mol. H_2O also seems to exist.

The sodium salt and lithium salt are obtained in the same manner, and both crystallise with 1 mol. H_2O. The sodium salt forms red, crystalline crusts, which are very soluble in water; sp. gr. 3·21.

All these salts are decomposed by water into iodates and chromic acid, but the decomposition is limited by the liberation of the chromic acid. The hydrated salts lose their water at 120—140°; at a higher temperature iodine and oxygen are given off, and a residue of dichromate is left. The solutions of these salts have an acid reaction, and when treated with alkalis or alkaline carbonates, yield a mixture of iodate and chromate. They readily give up oxygen to reducing agents, with formation of green chromic iodate together with some normal chromate and dichromate. Manganese, cobalt, and nickel form similar salts, but the corresponding salts of the alkaline earths do not appear to exist. C. H. B.

Structure of some Complex Inorganic Acids. By F. Kehrmann (*Ber.*, **20**, 1811—1813).—The author discusses certain constitutional formulæ for phosphomolybdates and phosphotungstates.

Phosphotungstic Acids. By F. Kehrmann (*Ber.*, **20**, 1805—1811).—When a cold concentrated solution of disodium tungstate (1 mol.) is mixed with aqueous phosphoric acid (4 mols.), a clear colourless liquid is obtained, which, when heated to boiling, turns yellow. On evaporation, after about three hours' boiling, and cooling, greenish-yellow plates separate. These consist of the sodium salts of at least three different phosphotungstic acids, which can be separated by conversion into the potassium salts followed by fractional crystallisation, for the details of which the original must be consulted. The derivative of one only of these acids is described.

α-Phospholuteotungstic acid, $H_5PW_8O_{29} + Aq$, is obtained in solution only by decomposing its silver salt with hydrochloric acid. The solution is colourless and strongly acid, and when evaporated turns yellow from formation of an anhydro-acid. The normal potassium salt forms small, white crystals; it is obtained by the action of hydrogen potassium carbonate on the potassium salt of the anhydro-acid. The normal *silver* salt, $Ag_5PW_8O_{29} + xAq$, is obtained as a pulverulent, yellowish-white precipitate. The normal ammonium salt, $(NH_4)_5PW_8O_{29} + xH_2O$, crystallises in sparingly soluble, lustrous, colourless tables.

α-Anhydrophospholuteotungstic acid, $H_3PW_8O_{28} + 16H_2O$, one of the three acids obtained as described above, is prepared by treating its potassium salt with hydrofluosilicic acid, or by evaporation of solutions of the hydrated acid. It crystallises in large, citron-yellow, six-sided, hexagonal or orthorhombic tables. It is a strong bibasic acid, yielding

readily soluble, yellow salts. The potassium salt, $K_3PW_8O_{28}$ + 20 (or 21) H_2O, barium salt, barium ammonium salt, $BaNH_4PW_8O_{28}$ + xAq, ammonium salt, $(NH_4)_3PW_8O_{28}$ + $20H_2O$, and silver salt, $Ag_3PW_8O_{28}$ + $20H_2O$, are described. A. J. G.

Physical Constants of Germanium and Titanium and their Compounds. By L. F. Nilson and O. Pettersson (*Chem. Centr.*, 1887, 329—330).—Determinations are given of the specific and atomic heats of germanium and titanium and its oxide, and of the vapour-densities, critical temperatures, and vapour-tensions of some of the compounds of germanium.

The atomic heats of germanium and titanium between the limits of temperature 100—0°, vary from 5·3—5·4, or about one unit less than the usual value; that of titanium increases with increase of temperature up to 7·77, at the temperature of sulphur vapour, whilst that of germanium remains constant.

Vapour-density determinations of germanium tetrachloride, tetraiodide, and monosulphide are in accordance with the formulæ $GeCl_4$, GeI_4, and GeS. The critical temperature of germanium chloride is 276·9. V. H. V.

Crystallised Compounds of Zirconium. By M. Weibull (*Ber.*, **20**, 1394—1396).—*Zirconyl chloride*, $ZrOCl_2$ + $8H_2O$, is obtained crystallised in prismatic needles from a hydrochloric acid solution of the so-called zirconium oxychloride. The crystals belong to the tetragonal system, and give $a : c = 1 : 0{\cdot}31816$. They are optically uniaxial, and show positive double refraction. *Zirconyl bromide*, $ZrOBr_2$ + $8H_2O$, yields similar tetragonal needles. *Zirconyl sulphate*, $Zr(SO_4)_2$ + $4H_2O$, is obtained by the slow evaporation of a solution containing free acid. The hexagonal plates belong to the rhombic system, and show $a : b : c = 0{\cdot}6326 : 1 : 1{\cdot}3350$. L. T. T.

Gold. By G. Krüss (*Annalen*, **238**, 241—275; continued from this vol., p. 450).—The atomic weight of gold is found to be 196·669, as the mean of 30 analyses of potassium aurobromide and of a neutral solution of auric chloride. The results obtained from the analysis of sublimed auric chloride are somewhat lower, and are rejected by the author on the grounds that the sublimed auric chloride probably contains traces of free chlorine.

The atomic weight of gold has recently been determined by Thorpe and Laurie (Trans., 1887, 565), who obtain the value 196·852.

W. C. W.

Alloys of Platinum, Iron, and Copper. By E. Maumené (*Bull. Soc. Chim.*, **47**, 39—41).—On heating 31·8 grams of platinum and 31·8 grams of iron with 66·6 grams of copper in a Perrot gas furnace, some of the iron remains unfused, but the fused portion of the metals forms a homogeneous alloy containing 7·43 per cent. of iron, 19·65 per cent. of platinum, and 72·92 per cent. of copper. This alloy is very readily oxidisable, being quickly covered with a coating of iron oxide and copper carbonate when exposed to the air.

A. P.

Crystalline Alloys of Tin and the Platinum Metals. By H. Debray (*Compt. rend.*, **104**, 1470—1472).—Platinum or an allied metal in the state of powder is fused in a porcelain crucible, with 20, 30, or even 50 times its weight of pure tin. Combination takes place with development of heat, and the alloy is allowed to cool slowly, and is then treated with dilute or concentrated hydrochloric acid, as the case may require.

The crystalline alloy of platinum and tin is only obtained by the action of very dilute hydrochloric acid on an alloy containing not more than 2 per cent. of platinum. The regulus dissolves gradually, and leaves a residue of brilliant lamellæ of the composition $PtSn_4$. With a stronger acid, or with a smaller proportion of tin in the regulus, the residue is variable in composition.

The alloy of tin and rhodium is obtained in small, brilliant crystals of the composition $RhSn_3$, by the action of slightly diluted hydrochloric acid at 0°, on a regulus containing 3 per cent. of rhodium. The crystals are not affected by cold, concentrated hydrochloric acid.

The iridium alloy is obtained in a similar manner from a regulus containing 6 per cent. of iridium. It forms small crystals of the composition $IrSn_3$, which are probably regular octahedra.

When the regulus obtained by fusing ruthenium with 10 times its weight of tin is treated with hydrochloric acid diluted with an equal volume of water, the alloy $RuSn_3$ is left in small, hopper-shaped crystals.

Osmium forms no similar alloy.

The alloys were analysed by heating them to bright redness in a current of hydrogen chloride, when the tin volatilises, or by heating to redness the alloy mixed with twice its weight of sodium chloride in a current of dry chlorine. C. H. B.

Action of Acids on Alloys. By H. Debray (*Compt. rend.*, **104**, 1577—1582).—The alloys of platinum and tin are somewhat readily attacked by hydrochloric acid even in the cold, whilst the alloys of tin with the other metals of the platinum group are not so readily affected (preceding Abstract).

The residues thus obtained form black scales which resemble graphite, and contain in addition to the platinum metal a considerable proportion of tin, together with small quantities of oxygen and hydrogen. Their composition, however, is very variable. They behave like platinum-black, developing more or less heat when placed in an atmosphere of hydrogen, and causing the detonation of explosive gaseous mixtures. The development of heat is not merely a result of the condensation of the hydrogen in the pores of the substance, but is partly due to the partial reduction of the metallic substance and the consequent formation of water. Probably many substances which are called "platinum-black" are of a similar nature, and act in a similar manner.

When the metallic residues are heated in a vacuum they lose water, and afterwards deflagrate without losing oxygen, and sometimes even become incandescent. They are more readily attacked by reagents than the metals which they contain. The residues from

the rhodium, ruthenium, and iridium alloys are partly dissolved by aqua regia, but the action is never complete. The rhodium residue alters even when dried in the air.

The residues still contain oxygen after having been heated in a vacuum, but they no longer have any catalytic properties.

The alloys of zinc with the platinum metals yield similar residues, but that from the platinum alloy itself contains neither oxygen nor hydrogen, and does not deflagrate when heated. The rhodium residue deflagrates violently, and is almost completely soluble in aqua regia.

The author has previously found that the alloys of the platinum metals and lead are attacked by dilute nitric acid, and yield black, explosive products (Abstr., 1880, 706).

The alloy of rhodium with copper is completely soluble in nitric acid, and the alloys of copper with the other platinum metals dissolve in notable quantity, but leave black, explosive residues which contain the platinum metal, copper, nitrogen, and oxygen, but are very variable in composition. The iridium residue is mixed with metallic iridium in the form of a crystalline powder, which indicates that some of the iridium dissolves in the copper, and separates out on cooling. C. H. B.

Mineralogical Chemistry.

Native Gold from Thibet. By A. Kalecsinszky (*Zeit. Kryst. Min.*, **13**, 73).—Native gold from East Thibet collected during Count Béla Széchenyi's expedition to Asia, gave on analysis the following results:—

Au.	Ag.	Cu.	Fe.	Total.	Sp. gr.
91·74	7·03	0·74	0·46	99·97	17·12

B. H. B.

Granular Limestones of Stainz in Styria. By E. Hussak (*Zeit. Kryst. Min.*, **13**, 52—54).—North-west of Stainz in Styria a bed of granular limestone containing felspar occurs in gneiss. The limestone contains microcline, albite, quartz, biotite, muscovite, tourmaline, hornblende, garnet, titanite, augite, and, occasionally, zoisite, zircon, chlorite, apatite, rutile, iron pyrites, magnetic pyrites, calcite, and, very rarely, orthoclase. With the exception of the microcline, all these minerals also occur in the gneiss enclosing the limestone.

An analysis of the microcline gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	Ignition.	Total.
64·55	19·75	trace	trace	13·97	1·91	0·25	100·43

The sp. gr. is 2·561. From its analogy to Becke's microperthite, the author regards the name of microcline-perthite as the most suitable for the Stainz felspar. B. H. B.

Manganese Apatite. Composition of Apatite. By M. Weibull (*Ber.*, **20**, 1525—1527).—Manganese apatite occurs in Westana, partly in reddish-brown masses, partly in crystals in pyrophyllite; the crystals are pale green, and more or less transparent; well-formed crystals are rare, sp. gr. = 3·225 at 17°. In the following series of numbers, the column A contains those obtained by analysis; B the same number less the amount of lime corresponding to that of fluorine; in C the relation of the atoms are given :—

	A.	B.	C.	
CaO.....	50·12	44·65	7·97	8·81
MnO.....	5·95	5·95	0·84	
P_2O_5.....	42·04	42·04	2·97	
F	3·64—3·84	3·74	1·97	
Cl.....	trace	trace	—	
Ca.....	—	3·91	0·98	

The numbers point to the formula $Ca_5(Mn)FO_9(PO)_3$ (comp. Völcker, Abstr., 1884, 162). N. H. M.

Celestine in Nautilus Aratus. By W. Stahl (*Chem. Zeit.*, **11**, 508—509).—The author has determined the composition of crystals found on the inner layer of a fossil *Nautilus aratus* from the Jura, near Rosswangen. The analysis gave—

SO_3.	BaO.	SrO.	CaO.
43·93	3·65	49·30	2·80

corresponding to the formula $BaCa_2Sr_{20}(SO_4)_{23}$; the specific gravity of the crystals was 3·91. J. P. L.

Artificial Formation of Alabandine. By H. Baubigny (*Compt. rend.*, **104**, 1372—1373).—1·1 gram of manganese sulphate was dissolved in 150 c.c. of water, mixed with a slight excess of ammonium acetate and a few drops of acetic acid, saturated at 0° with hydrogen sulphide, and sealed up in glass tubes. After remaining at the ordinary temperature from four or five years, distinct, dark green, octahedral crystals were formed. These were not analysed, but there can be little doubt that they are alabandine or crystallised manganous sulphate. C. H. B.

Artificial Production of Crocoisite. By L. Bourgeois (*Compt. rend.*, **104**, 1302—1303).—When lead chromate is heated with nitric acid diluted with 5—6 vols. of water, and the clear liquid decanted or filtered, it deposits crystals of lead chromate as it cools. The best results are obtained when the liquid is heated in sealed tubes, excess of lead chromate being avoided. The crystals are brilliant, deep orange-red, monoclinic prisms, which become crimson and then deep purple when heated, but regain their original colour on cooling. In crystalline form, optical properties, and other physical and chemical properties, the crystals are identical with crocoisite; sp. gr. = 6·29. C. H. B.

Långbanite, a new Swedish Mineral. By G. Flink (*Zeit. Kryst. Min.*, **13**, 1—8).—This mineral occurs at Långbanshyttan, in Wermland, in association with schefferite, and appears to be extremely rare. An analysis of 0·4117 gram gave the following results:—

SbO_2.	SiO_2.	Mn_3O_4.	Fe_2O_3.
0·0603	0·0448	0·2934	0·0472

The other substances were present in quantities too small to be estimated. The finely-powdered mineral was soluble in warm hydrochloric acid, no chlorine being given off. It may, therefore, be assumed that the iron and manganese are present as protoxides. The analysis would then be—

Sb_2O_5.	SiO_2.	MnO.	FeO.	Total.
15·42	10·88	64·00	10·32	100·62

The formula suggested is $37Mn_5SiO_7 + 10Fe_3Sb_2O_8$.

The mineral occurs only in the form of crystals. They belong to the hexagonal system; the axial ratio being $a : c = 1 : 1·6437$. The following planes were determined with certainty:—Base, 0P; prisms, ∞P, ∞P2; protopyramids, P, $\frac{1}{2}$P, 2P; deuteropyramids, $\frac{1}{3}$P2, $\frac{2}{3}$P2, $\frac{4}{3}$P2; dihexagonal pyramids, $3P\frac{3}{2}$, $\frac{5}{6}P\frac{5}{4}$.

The colour of the mineral is an iron black with metallic lustre. It has a hardness of 6·5 and a sp. gr. of 4·918. B. H. B.

Mineralogical Notes. By A. H. Chester (*Amer. J. Sci.*, **33**, 284—291).—1. *Fuchsite.*—This variety of mica occurs on Aird Island, in the district of Algoma, Canada, in a coarsely crystalline dolomite. An analysis of a pure sample, carefully separated from the accompanying mica, gave the following results:—

SiO_2.	Al_2O_3.	Cr_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
45·49	31·08	3·09	0·51	3·36	9·76	0·90	5·85	100·04

The occurrence of chrome mica in Canada has been mentioned by Dawson; but no analysis has heretofore been published. The dolomite in which the fuchsite occurs is interesting on account of its peculiar appearance, which causes it to be readily mistaken for calcite. Analysis shows it to be a true dolomite in which part of the magnesium carbonate is replaced by iron carbonate.

2. *Pink Celestine.*—Celestine occurs at the stone quarries near Lairdsville in masses of prismatic crystals. It is interesting on account of its colour, which is usually pink, although sometimes the mineral has the ordinary blue tint. Analysis gave the following results:—

SrO.	BaO.	CaO.	SO_3.	SiO_2.	Total.
46·71	7·28	2·01	43·20	0·28	99·48*

3. *Zinkenite.*—This rare mineral has been discovered with antimony ores at the Stewart Mine, Sevier Co., Arkansas.

* 100·38 in original.

4. *Brochantite.*—A specimen of this mineral from Chili gave on analysis the following results, after deducting 4·45 per cent. of insoluble matter:—

CuO.	SO_3.	H_2O.	Total.
71·73	18·21	10·06	100·00

5. *Pectolite.*—A specimen of the so-called okenite from Disco Island gave on analysis—

SiO_2.	CaO.	Al_2O_3.	Na_2O.	K_2O.	H_2O.	Total.
52·86	34·33	0·71	7·50	0·47	4·70	100·57

This is evidently pectolite, and probably resembles much that is called okenite from the same locality.

6. *Scorodite.*—This rare mineral has been found at the Horn Silver mine, at Frisco, Utah. A pure sample for analysis could not be obtained. Before the blowpipe, the mineral gives the reactions of arsenic acid, iron, and water.

7. *Bismuthite.*—A mineral from Casher's Valley, North Carolina, proved to be bismuthite. The analysis gave the following results:—

BiO_2.	CO_2.	H_2O.	Insoluble.	Total.	Sp. gr.
86·36	7·79	2·02	3·63	99·80	7·45

The formula suggested is $Bi_2C_3O_9 + 2Bi_2H_2O_4$. Comparing this formula with that given by Weisbach for his bismutosphærite, it is found that they differ only in the hydration of the bismuth oxide. A new examination of bismutosphærite appears desirable, for it is curious that the loss in the analysis should be exactly equal to the amount of water required to make it the well-known mineral bismuthite.

8. The author also describes some hemimorphic crystals of barytes from De Kalb, St. Lawrence Co., New York, and some interesting pseudomorphs of cerargyrite after pyrargyrite occurring at the Horn Silver Mine, Frisco, Utah. B. H. B.

Minerals of the Serpentine-Chlorite-group. By V. Wartha (*Zeit. Kryst. Min.*, **13**, 71—72).—The author gives analyses of two rocks he found in the Montafun Valley, Vorarlberg. The first came from Grandau (Analysis II), and resembles serpentine. The second came from Tafamunt (Analysis III), and resembles chlorite-schist. As the Grandau rock closely resembles the so-called *precious serpentine* from Borostyánkö in Eisenburg County, West Hungary, the author also gives an analysis of this (Analysis I). The analytical results were as follows:—

	SiO_2.	FeO.	Fe_2O_3.	Al_2O_3.	MgO.	H_2O.	CaO.	Total.	Sp. gr.
I.	30·45	3·70	2·21	18·96	32·20	12·79	—	100·31	2·693
II.	29·44	5·60	2·00	20·98	30·31	12·29	—	100·62	2·722
III.	39·83	6·22	11·78	4·43	26·87	8·23	2·32	99·68	2·876

From these results, the author concludes that the Hungarian rock

and that from Grandau are identical with Kenngott's pseudophite, whilst the Tafamunt rock is serpentine-schist.

In conclusion the author gives a number of analyses of serpentines free from alumina, and compares them with the analyses of minerals of the pennine, ripidolite, and chlorite-groups. He concludes that the typical serpentine (massive serpentine from Zermatt and from Windisch Matrey) contains a certain quantity of alumina, and that, with reference to the percentage of alumina, there is always observable a transition from serpentine to pennine. Serpentine, in fact, is nothing else than a characteristic member of the chlorite-group, in which the percentage of alumina is eventually equal to nought.

B. H. B.

Imperfectly known Silicates. By E. Schluttig (*Zeit. Kryst. Min.*, **13**, 73—76).—*Glaucophane.*—An analysis of the glaucophane, described by A. v. Lasaulx, from the Pointe des Chats, Brittany, gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
I.	56·65	12·31	3·01	4·58	2·20	12·29	1·05	7·93	100·02
II.	57·13	12·68	8·01		3·34	11·12	trace	7·39	99·67

A. v. Lasaulx' results (II) are added for purposes of comparison.

Violan from St. Marcel in Piemont gave on analysis the following results:—

SiO_2.	Al_2O_3.	FeO.	NiO + CoO.	MnO.	CaO.	MgO.	K_2O.
52·02	2·60	0·80	0·39	2·87	22·94	15·18	0·75

Na_2O.	Total.	Sp. gr.
4·94	102·49	3·231

The mineral was of a violet colour, and was associated with quartz, tremolite, and piemontite.

Sapphirine from Fiskenäs in Greenland gave on analysis the following results:—

SiO_2.	Al_2O_3.	FeO.	MgO.	Total.
14·76	63·23	1·65	19·75	99·39

This agrees with Rammelsberg's formula $(MgFe)_5Al_{10}Si_2O_{23}$.

Felspar in the Corsican Diorite.—This has hitherto been regarded as anorthite. The author concludes that it is a labradorite, composed of albite (1 mol.) and anorthite (3 mols.) His analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
47·38	29·58	1·34	12·26	1·50	3·15	2·14	2·33	99·68	2·70

B. H. B.

Plagioclase from Tynemouth Dyke. By J. J. H. Teall (*Zeit. Kryst. Min.*, **13**, 96).—An analysis of a specimen of plagioclase from the rock of a North-of-England dyke gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Loss.	Total.
47·30	31·50	1·85	14·88	0·93	0·38	1·22	1·80	99·86

The crystals are porphyritic, and glassy in texture. A section parallel to the basal plane gave 55° 10′ as the angle between the extinction positions of adjacent lamellæ. The corresponding angle in anorthite lies between 57° and 74°, and in labradorite between 10° and 14° 30′. B. H. B.

Action of Heat on Clays. By H. Le Chatelier (*Compt. rend.*, **104**, 1443—1446).—The author has investigated the behaviour of clays on heating with a view to determine their constitution, and if possible to devise a scheme of classification. The temperatures were measured by means of a thermoelectric couple consisting of pure platinum, and platinum containing 10 per cent. of rhodium, and were registered photographically by means of a reflecting galvanometer.

It was found that when small quantities of clay are heated the rate of increase of temperature slackens considerably at the moment of dehydration, and this point can be used as a means of distinguishing between different classes of hydrated silicates. The position of this point is independent of the conditions and notably of the rapidity of heating. The phenomenon is due to the fact that as soon as the velocity of a chemical change attains a notable value it increases very greatly for small increments of temperature. During the heating of the clays, however, there is not only a reduction in the rate of increase of temperature due to dehydration, but sudden accelerations are observed which indicate the occurrence of changes accompanied by a development of heat.

The examination of a large number of clays shows that these substances are much less complicated than was believed. They may be divided into five well-defined groups, typical members of which are halloysite from Miglos; allophane from Saint Antoine; kaolin from Red Mt., Colorado; pyrophyllite from Beresow, and montmorillonite from St. Jean de Cole respectively. The first group shows a feebly marked reduction in the rate of increase at 150—200°; a second well-marked reduction ending at 700°, followed by an acceleration at 1000°. The second shows well-marked reduction at 150—220°, followed by acceleration at 1000°. The third shows a reduction at 770°, followed by a slight acceleration at about 1000°. The fourth shows a well-marked reduction ending at 700°, and a second less strongly marked reduction at 850°. The fifth shows a well-marked reduction at 200°, a second less strongly marked at 770°, and a doubtful reduction at 950°. C. H. B.

Constitution of Clays. By H. Le Chatelier (*Compt. rend.*, **104**, 1517—1520).—When hydrated silica is gently heated it shows a diminution of the rate of increase of temperature between 100° and 200°. Alumina under the same conditions behaves differently according to the method by which it has been prepared. If precipitated from sodium aluminate it shows a first diminution below 200°, and a second ending at 360°; if precipitated from aluminium salts or prepared by calcination of the nitrate at a moderate temperature it shows the same reductions followed by a sudden acceleration in the rise of temperature at 850°; bauxite shows a diminution at 700°.

From these facts it follows that the author's experiments (preceding Abstract) cannot be taken as showing the presence of free silica in clays, and they indicate that the first two hydrates of alumina cannot exist in any of the clays examined, whilst the hydrate present in bauxite can only be present in halloysite if in any. The evolution of heat at high temperatures is due to a molecular change in the alumina, which beyond this point becomes insoluble. Free alumina does not exist in clays, but is liberated by their decomposition on dehydration.

Clays belonging to the montmorillonite-group have the composition $4SiO_2,Al_2O_3,H_2O$ + Aq, whilst halloysites have the composition $2SiO_2,Al_2O_3,2H_2O$, and in this respect are identical with kaolin. They are, however, distinguished from the latter by their behaviour during dehydration, and their solubility in acids after heating.

C. H. B.

River Waters of La Plata. By R. Schoeller (*Ber.*, **20**, 1784—1788).—I. La Plata water near Buenos Ayres. Water of brownish colour and slightly turbid. II. Uruguay water, from about 3 miles above Fray Bentos; it was of pale brown colour and slightly turbid. III. Rio Negro water from above Mercedes; it was clear and nearly colourless. The results of the analyses of the filtered waters were as follows (grams per kilo.).

	I.	II.	III.
Organic matter	0·09	0·052	0·075
Total residue dried at 180°	0·2075	0·087	0·1394
Loss on ignition	0·026	0·0248	0·034
Na_2O	0·0691	0·0053	0·01816
CaO	0·0107	0·0093	0·03281
MgO	0·00486	0·0032	0·00431
Al_2O_3	0·0099	0·0008	0·002
Fe_2O_3		0·0018	
SO_3	0·03085	0·0034	0·00135
SiO_2	0·0223	0·0294	0·0286
Cl	0·0373	0·0034	0·00583
N_2O_5	0·0128	—	trace
N_2O_3		—	0·00224
P_2O_5	—	—	trace
CO_2 (combined)	0·0175	0·0105	0·03771
CO_2 (free or half combined)	—	0·037	—

Potassium was not detectable with the spectroscope in any of the waters.

A. J. G.

Organic Chemistry.

Iodoform and Bromoform. By F. Günther (*Arch. Pharm.* [3], 25, 373—394).—Most of the methods given in text-books for the preparation of bromoform yield either none of that compound or very little. Methyl alcohol under the action of alkali and bromine gives no bromoform unless the alcohol be impure, formic acid being obtained. Ethyl alcohol under the same conditions gives acetic acid. If, however, the compound analogous to bleaching powder is prepared with bromine and milk of lime, this when heated with ethyl alcohol and then distilled gives bromoform. The best raw material is acetone. This when mixed with ten times its weight of a 20 per cent. soda solution heated at 50°, and treated with bromine in the smallest possible portions at a time, gives a yield of 81 per cent. of the theoretical amount of bromoform. The process goes quietly but lasts for some days. Caustic alkali in place of the carbonate accelerates the process, but the yield falls to 62·5 per cent. Acetaldehyde in presence of an alkali and bromine gives no bromoform.

Anhydrous aldehyde under the action of bromine gives as one product a substance having the empirical formula $C_4H_7BrO_2$, but whose constitution is quite uncertain; when heated with aqueous alkalis it yields bromoform and what seems to be a true resin.

Iodoform.—Alcohol containing 20 to 25 per cent. aldehyde is the most suitable raw material for the production of this compound. It is mixed with ten times its weight of soda solution, iodine is added, and the mixture stirred round from time to time; the iodoform gradually and quietly separates out. The process is completed in the cold. Some sodium iodide may be added with advantage, to increase the solubility of the iodine. As bye-product, sodium iodide nearly free from iodate is obtained. J. T.

Products from the Residues of Compressed Gas. By A. Colson (*Compt. rend.*, 1286—1289).—The residues from compressed gas were heated at about 35°, and one part of the evolved gases was condensed in a flask by means of a freezing mixture, whilst the remainder was absorbed by bromine, the bromides being afterwards fractionated. The fraction boiling at 148° is isobutylene bromide, about 100 grams being obtained from 6 litres of gas oil. The fraction at 156—159° is smaller, and consists of diethylidene bromide, but the greater quantity of the brominated product consists of ethylvinyl bromide boiling at 167°.

The portion of the gas condensed by the freezing mixture contains a certain quantity of the three butylenes, but consists mainly of hydrocarbons richer in carbon (b. p. 11—30°), and when treated with bromine yields the erythrene bromide described by Caventou. This bromide is soluble in boiling concentrated nitric acid, and is deposited unchanged on cooling. It is very slightly attacked at 180° by a solution of lead acetate in benzene. If powdered silver nitrate is

added to the nitric acid solution, silver bromide is precipitated, but even after boiling for half an hour the decomposition of the erythrene bromide is not complete. If the acid liquid is then poured into cold water, a yellow oil of the composition $NO_2{\cdot}C_4H_5Br_2(NO_3)_2$ separates; sp. gr. 1·800.

Aniline reacts energetically with erythrene bromide, and forms the base $C_4H_6Br_2(NHPh)_2$, which melts at 62°, and is soluble in ether, but almost insoluble in water. It is coloured reddish-brown by nitric acid, and dissolves in hydrochloric acid, but is precipitated unchanged when the latter is mixed with water.

Orthotoluidine also reacts with erythrene bromide.

Ethylene bromide reacts with aniline, and forms the base $C_2H_4(NHPh)_2$ described by Hofmann. With orthotoluidine it yields *ethyleneditolyldiamine*, $C_2H_4(NC_7H_8)_2$, which is separated from orthotoluidine by adding excess of hydrobromic acid. The hydrobromide is somewhat soluble in boiling water containing hydrobromic acid, and separates on cooling. It is partially decomposed by pure boiling water; ammonia precipitates the base from the solution. Ethyleneditolyldiamine is a white, crystalline solid which melts at 72°. It dissolves in 7 parts of ether and 10—12 parts of alcohol, the solubility in both cases increasing with the temperature. It also dissolves in 300 parts of boiling water. It has very little taste; its alcoholic solution reacts with methyl-orange, but not with phenolphthaleïn.

Ethylenediphenyldiamine reacts with indicators, both in alcoholic and aqueous solutions. Its hydrochloride, $C_2H_4(NPh_2),2HCl$, is bitter, and only slightly soluble in water. C. H. B.

Caprylidene: Constitution of Capraldehyde. By A. Béhal (*Bull. Soc. Chim.*, **47**, 33—39).—The compound $C_8H_{16}O$ obtained on distilling neutral sodium ricinoleate, when treated with phosphoric chloride, yields octylene chloride, and this when boiled for 72 hours with alcoholic potash in a reflux apparatus yields chloroctylene and a little octylidene. The chloroctylene, $C_8H_{15}Cl$, separated on the addition of water to the alcoholic solution, is heated with alcoholic potash in a sealed tube at 150° for 12 hours. Water is then again added, and the oily liquid which separates is fractioned; the portion boiling between 130° and 136° contains the *caprylidene;* this hydrocarbon, C_8H_{14}, is evidently a member of the acetylene series, as it yields characteristic precipitates with cuprous chloride and silver nitrate solutions. It may be converted into methyl hexyl ketone by adding it very gradually to well-cooled sulphuric acid which is kept constantly agitated, the liquid darkens and sulphurous anhydride is given off, the mixture is then poured on a sufficient quantity of ice to reduce the temperature considerably when an oily layer separates, the mixture is next neutralised with sodium carbonate and distilled; the distillate coming over first with the vapour of water is dried over calcium chloride and again fractioned; thus prepared *methyl hexyl ketone* has an agreeable odour somewhat like that of apples. It boils at 171° under 761·7 mm. pressure, sp. gr. at 0° = 0·8351; it is insoluble in water, but dissolves readily in alcohol and ether, does not

reduce either an ammoniacal solution of silver nitrate nor Fehling's solution, but forms a combination with hydrogen sodium sulphite which is decomposed again by hot water; on oxidation of the ketone with chromic mixture, caproic and acetic acids are formed. From the above results the author considers that the view held by Staedeler and Pettersen (*Ann. Chem. Phys.*, **118**, 78), that the compound $C_8H_{16}O$ obtained on distilling sodium ricinoleate is a methyl hexyl ketone is clearly shown to be erroneous, and that the compound produced is in fact capraldehyde, differing altogether in properties from the methyl hexyl ketone which may be prepared from it. A. P.

Erythrene Bromides. By E. Grimaux and C. Cloez (*Compt. rend.*, **104**, 1446—1448).—Whatever its origin, erythrene tetrabromide (see this vol., p. 352) melting at 115—116° distils easily in the vapour of water. The anhydrous compound distils completely at 260—270° with evolution of very little hydrogen bromide, and formation of a small, carbonaceous residue. When the distillate is treated with light petroleum, in which the tetrabromide is only very slightly soluble, and the petroleum is allowed to evaporate, it deposits bulky, transparent, tabular crystals which melt at 37·5°, but have the same composition as the crystals melting at 115—116°, and yield the same products with alcoholic potash. It may be assumed that the tetrabromide splits up into hydrogen bromide and the derivative $CH_2 : CBr{\cdot}CBr : CH_2$, which afterwards recombine, forming the compound $CH_3{\cdot}CBr_2{\cdot}CBr_2{\cdot}CH_3$. This compound was obtained by Ciamician and Dennstedt from erythrene derived from pyrroline, but they regarded it as a direct product of the action of bromine, whereas its formation was really due to the fact that they purified their tetrabromide by distillation in a vacuum.

Both forms of tetrabromide when treated with alcoholic potash yield dibromerythrene, which however only exists in alcoholic or ethereal solution, and polymerises rapidly even in the dark when separated from its solvents. It combines readily with bromine to form dibromerythrene dibromide, which crystallises from ether in slender needles melting at 67°, and is very soluble in alcohol or ether. It combines slowly with excess of bromine, forming the tetrabromide $C_4H_4Br_2Br_4$, which crystallises in brilliant, nacreous plates melting at 170° with decomposition. It is slightly soluble in ether.

When the more volatile portion of the oil from compressed gas is treated with a limited quantity of bromine, it yields butylene bromide, together with a small quantity of erythrene dibromide which boils between 190° and 200° but has not yet been isolated. C. H. B.

Free Thiocyanic Acid and Cyanuric Acid, and their Compounds with Ethers and Alcohols. By P. Klason (*J. pr. Chem.* [2], **35**, 400—413).—The preparation of free thiocyanic acid has been described by Wöhler, Liebig, and Hermes; the present work refers to its decompositions. Hydrogen chloride has no action whatever, even at 100°, on potassium thiocyanate; but when passed into the fused salt, it acts rapidly, a volatile liquid consisting of carbon bisulphide and hydrocyanic acid, a yellow-red sublimate consisting

essentially of persulphocyanic acid and dithiocyanic acid, and a residue of ammonium chloride, melamine and unaltered potassium cyanate being obtained. On mercuric thiocyanate, hydrogen sulphide has but little action, but hydrogen chloride acts readily with formation of a white sublimate. A 10 per cent. aqueous solution of thiocyanic acid when distilled in a vacuum, and the vapours dehydrated by passing over calcium chloride at 40°, yields an acrid and very volatile distillate, which when taken from the freezing mixture becomes hot and solidifies. For the preparation of the aqueous acid, the methods of Vogel and Sommering, and of Hermes, are not suitable; it is most easily obtained by decomposition of barium thiocyanate with sulphuric acid. Although the aqueous acid cannot be distilled under ordinary conditions without decomposition, yet on distillation in a vacuum an acid of 10 per cent. suffers no decomposition; and an acid of even 30 per cent. may be obtained by distilling in a vacuum a mixture of potassium thiocyanate and hydrochloric acid, both in strong aqueous solution. An acid of less than 5 per cent. may be preserved; stronger acids can only be kept at low temperatures; when free from polymerisation products they give no precipitate with iodine solution; when distilled the acid comes over first. An aqueous acid shaken with ether yields almost all its acid to the ether; on distillation the ether passes over until the residue contains 30 to 36 per cent. of acid, after which the acid begins to decompose; but distilled in a vacuum it passes over unaltered, and after treatment with calcium chloride contains equal molecules of ether and thiocyanic acid; the vapour-density corresponds to a mixture of the two components, the vapour is not altered by heating at 100°, but decomposes on cooling. The free acid is therefore stable only in weak aqueous solution, or as a vapour. A compound of thiocyanic acid and methyl alcohol is obtained by passing hydrogen chloride into a solution of ammonium thiocyanate in methyl alcohol, and distilling in a vacuum; by fractional distillation a liquid of constant boiling point is obtained, consisting of two molecules of methyl alcohol to one of thiocyanic acid. An exactly similar ethyl compound is obtained in like manner, and an aqueous solution of the free acid when shaken with amyl alcohol yields a solution which after fractionation in a vacuum contains almost three molecules of the alcohol to one of the acid.

Cyanic acid is also absorbed by ether, and on distilling the temperature gradually rises, but a substance of constant composition could not be isolated. It is considered that when cyanic acid acts on alcohols, compounds are first formed similar to those yielded by thiocyanic acid, and that the urethanes are products of their decomposition.

H. B.

Action of Polyatomic Alcohols on Solutions of Boric Acid and Hydrogen Sodium Carbonate. By C. Jehn (*Arch. Pharm.* [3], **25**, 250—251).—R. Sulzer has recently shown that solutions of boric acid and hydrogen sodium carbonate do not react on each other, but that the addition of glycerol or honey causes a reaction resulting in the evolution of carbonic anhydride. Normal carbonate gives no reaction under like conditions. Borax behaves like boric acid with

both hydrogen and normal carbonate. Also Sulzer showed that cane-sugar and milk-sugar do not induce reaction, whilst grape-sugar causes reaction. The action of honey is doubtless due to the presence of grape-sugar. Thus the reaction is induced by a triatomic alcohol, glycerol, and the aldehyde of a hexatomic alcohol, glucose. Hence it became of interest to ascertain if other polyatomic alcohols and their corresponding aldehydes possessed similar power. Mannitol caused reaction between boric acid and hydrogen sodium carbonate; but not in the case of borax and the salt. Erythrite, a tetratomic alcohol, behaved like mannitol. J. T.

Sugar Compounds. By W. Stromeyer (*Arch. Pharm.* [3], **25**, 229—245).—Some of the saline compounds formed by the action of the sugars on certain bases have been repeatedly examined with conflicting results. The barium, calcium, and lead compounds were again examined. The author shows that the barium salt is an additive product of one molecule of cane-sugar with one molecule of barium oxide, $C_{12}H_{22}O_{11},BaO$, thus confirming the view previously expressed by Peligot, Soubeiran, and Gerhardt. A similar monocalcium compound, $C_{12}H_{22}O_{11}CaO$, was prepared by Peligot's method, in which freshly ignited calcium oxide is added to an excess of sugar in solution, and the salt is precipitated by the addition of alcohol. A tricalcium compound was prepared as indicated by Peligot, namely, by boiling the aqueous solution of the monocalcium compound. This was found to have the formula $C_{12}H_{22}O_{11},3CaO$, thus agreeing with the views of Peligot, Daniell, and E. v. Lippmann. The lead compound on the contrary appears to be a substitution-product approaching in composition to $C_{12}H_{18}Pb_2O_{11}$, as maintained by Peligot, Soubeiran, and Mulder. This may arise from the facility with which basic compounds of organic lead salts are formed. An attempt to obtain an aluminium compound was unsuccessful. Chromium oxide was also found to be only slightly soluble in sugar solution. J. T.

Formation of Galactose and Lævulose from Raffinose. By J. Haedicke and B. Tollens (*Annalen*, **218**, 308—318).—When raffinose is boiled for some hours with dilute sulphuric acid, it is converted into galactose and lævulose. On treating with sodium amalgam the mother-liquor from which the galactose has been deposited, a mixture of dulcitol and mannitol is obtained. W. C. W.

Galactose from Carragheen Moss. By J. Haedicke, R. W. Bauer, and B. Tollens (*Annalen*, **238**, 302—307).—Carragheen moss, the dried algæ *Chondrus crispus*, yields on extraction with water containing 0·6 per cent. SO_3, and on further purification with alcohol, a small quantity of a crystalline compound which resembles galactose in its composition, action on polarised light, and its behaviour with nitric acid. On oxidation with nitric acid, the dry moss yiel ls about 21·6 to 22·2 per cent. of mucic acid; almost the same yield is obtained from raffinose. W. C. W.

Saccharification of Starch by Nitric Acid. By A. Seyberlich and H. Trampedach (*Chem. Centr.*, 1887, 346—347).—The saccharification of starch by nitric acid has not as yet proved successful, as the product retains a considerable quantity of the syrup, and with it the soluble metallic salts which impart a saline taste to the sugar. The process adopted by the authors, by means of which the syrup is removed from the crystals, is as follows:—Dry starch is stirred with twice its weight of water to form an emulsion, and one two-hundredth of its weight of nitric acid added. The boiling process is conducted in a wooden vessel provided with reflux condensers; the syrup is neutralised with chalk, sodium carbonate added to slight alkaline reaction, and then evaporated to crystallisation in a vacuum. From this alkaline solution the sugar separates in small, individual crystals which do not retain the syrup. When crystals are no longer obtainable from the syrup, sulphuric acid is added in sufficient quantity to convert the calcium nitrate into sulphate, and after separation of the latter the liquid can be used in a succeeding operation.

V. H. V.

Nitrocellulose. By F. Nettlefold (*Chem. News*, **55**, 306).—The nature of the fibre influences the degree of nitration in nitrocellulose preparations. Thus whilst cotton attains 13·94 per cent. nitrogen, or very nearly the theoretical proportion in trinitrocellulose, pine flour and wood pulp reach only 11·2. But in these last instances, and in others mentioned in the paper, the product is divisible by solvents into different fractions with proportions of nitrogen that indicate the existence of nitro-compounds more complicated than di- and tri-nitrocellulose.

R. R.

Amines in Suint. By A. Buisine (*Compt. rend.*, **104**, 1292—1293).—A fresh aqueous extract of suint contains very little ammonia, but after standing for some time the proportion of this alkali increases considerably. It results from the decomposition of urea, exists in the form of carbonate, and is completely expelled by boiling. In addition to ammonia, the vapour given off when the solution is boiled contains monomethylamine and trimethylamine, the proportion between the three alkalis being ammonia 95, monomethylamine 4, trimethylamine 1.

C. H. B.

Trimethyl-α-amidobutyrobetaïne. By E. Duvillier (*Compt. rend.*, **104**, 1520—1522).—This compound is obtained by the action of ethyl bromobutyrate (1 mol.) on an alcoholic solution of trimethylamine (1·5 mol.). When the liquids are mixed, a precipitate is at once formed, but no heat is developed. The liquid is heated in closed tubes at 100° for about 12 hours, treated with barium hydroxide, distilled, the barium precipitated exactly with sulphuric acid, and the filtrate treated with silver oxide and concentrated. A syrupy alkaline liquid is obtained, which eventually becomes solid, and when this is treated with alcohol and the soluble product recrystallised from alcohol, *trimethyl-α-amidobutyrobetaïne*, $CH_2Me{\cdot}CH<^{-CO-}_{NMe_3}>O$ + H_2O, is obtained in bulky, transparent crystals, which become anhydrous at 120°. It is extremely soluble in water, very soluble in

alcohol, but insoluble in ether; it has a neutral reaction and a bitter taste.

The mother-liquor contains tetramethylammonium hydrate, together with the betaïne, and by addition of platinic chloride and systematic crystallisation the two compounds can be separated. *Trimethyl-α-amidobutyrobetaïne platinochloride* forms elongated, pointed, orange-yellow prisms, which are almost insoluble in alcohol; they contain 1 mol. H_2O, but become anhydrous at 100°. The *hydrochloride* is obtained from the platinochloride, but will not crystallise. If its solution is mixed with auric chloride, a precipitate seems to form, but this is really an emulsion of the aurochloride, which after some time separates as a yellow oil; this dissolves readily on heating, but is reprecipitated as an oil when the liquid cools. After some time it solidifies and forms lamellar crystals.

Attempts to obtain the corresponding ethyl-derivative were unsuccessful. A small quantity of triethyl-α-amidopropiobetaïne was, however, obtained by the action of ethyl-α-amidopropionate on triethylamine. C. H. B.

Action of Ammonia on Chlorethanes: Direct Union of Ammonia with Non-saturated Compounds. By R. Engel (*Compt. rend.*, **104**, 1621—1624).—Vinyl chloride, obtained by treating ethylene chloride with alcoholic potash, was washed with alcohol, and passed into alcoholic ammonia until no more was dissolved. At the ordinary temperature there is no action, even after several months. Vinyl bromide likewise has no action on alcoholic ammonia at the ordinary temperature. At 100° there is also practically no action, but at 150—160°, in presence of concentrated alcohol, a complex reaction takes place, the principal product being ethylenediamine. This result shows that certain non-saturated compounds are capable of combining directly with ammonia, a reaction which furnishes a new method of preparing amines. The author has obtained several acid amines by the action of ammonia on non-saturated acids.

In all cases when ammonia acts on ethylene chloriodide in aqueous or alcoholic solution, only ethylene bases are formed, both halogens being removed simultaneously. These results agree with Simpson's observations. Friedel and Silva have likewise shown that when ethylene chloriodide is treated with silver the products are ethylene and ethylene chloride.

Ammonia acts more readily on chlorethylene chloride in either alcoholic or aqueous ammonia even at the ordinary temperature. The product is always $C_2H_2Cl_2$, boiling at 37°, and hence the action of ammonia under these conditions is similar to that of potash. The theoretical yield is obtained. C. H. B.

Red Dye from Chloral Hydrate. By J. Z. Lerch (*Chem. Centr.*, 1887, 299).—Walz, Ogston, and others have noticed the formation of red colouring matter of the composition $C_{18}H_{24}S_{13}N_4O_6$ when ammonium sulphide is added to chloral hydrate. If hydrogen sulphide is passed into an ammoniacal solution of chloral hydrate a larger amount of the dye is produced. On prolonged passage of the

gas the red passes into a yellow coloration simultaneously with the disappearance of the alkaline reaction. A good result is obtained with sodium thioantimonate, the liquid becoming turbid with separation of sulphur and antimony pentasulphide. This reaction can be used for the detection of chloral hydrate. After acidification, the red colouring matter can be taken up by petroleum, chloroform, and carbon bisulphide to form yellow solutions, turning red on addition of alkali. From the solution in petroleum, the compound is obtained in fine crystals of a green, metallic lustre. Salts of mercury, lead, and silver form red compounds with solutions of the crystals, which decompose slowly after a time, but more rapidly on heating, with separation of metallic sulphides. V. H. V.

Condensation of Normal Butyraldehyde. By G. A. Raupenstrauch (*Monatsh. Chem.*, **8**, 108—119).—*α-Ethyl-β-propylacrylic aldehyde*, $CH_2Me\cdot CH_2\cdot CH:CEt\cdot CHO$, is prepared by adding 35 grams of 10 per cent. aqueous soda to a mixture of 35 grams of normal butyraldehyde and 600 c.c. of water. The whole is shaken and heated for two hours at 40°. After 24 hours it is made neutral or slightly acid by dilute sulphuric acid, and steam-distilled in an atmosphere of carbonic anhydride. The oily product is dried and distilled in a current of carbonic anhydride. It is a colourless oil boiling at 172·4—173·4° (corr.); it is almost insoluble in water, insoluble in hydrogen sodium sulphite. It reduces ammoniacal silver solution, and reacts with phenylhydrazine. When treated with bromine the compound $C_8H_{14}Br_2O$ is formed. When oxidised with potassium dichromate and sulphuric acid, an acid, $C_8H_{16}O_2$, is obtained.

Ethylbutylacetaldehyde, $C_4H_9\cdot CHEt\cdot CHO$, is obtained by reducing the above aldehyde with iron filings and 60 per cent. acetic acid; the product is distilled, and the fraction boiling below 179° treated with sodium hydrogen sulphite, and the crystalline double compound washed with ether and decomposed by sodium carbonate. It is then steam-distilled. It is an oily substance, boiling at 160—162° (uncorr). It reduces ammoniacal silver solution, and does not form an additive compound with bromine. The portion of the product which boils above 179° appears to consist of an unsaturated alcohol, $C_7H_{13}\cdot CH_2\cdot OH$, and the corresponding saturated octyl aldehyde. N. H. M.

Glyceraldehyde. By E. Grimaux (*Compt. rend.*, **104**, 1276—1278).—Anhydrous glycerol oxidises somewhat rapidly in contact with comparatively inactive platinum-black, and if the platinum is very active it is necessary to dilute the liquid with about 2 vols. of water in order to moderate the energy of the reaction. The liquid acquires considerable reducing power and becomes acid, the acidity increasing as the reducing power diminishes if the action of the platinum is prolonged, owing to the conversion of the aldehyde into the acid. The product is extracted with water and the solution concentrated in a vacuum. It reduces Fehling's solution, gives a mirror with ammonio-silver nitrate, and becomes yellow when boiled with alkalis, lime, or baryta. If the concentrated solution is mixed with sodium hydrogen sulphite, heat is developed, and on addition of alcohol

a gummy mass is precipitated which seems to be a combination of the sulphite and glyceraldehyde. With phenylhydrazine hydrochloride and sodium acetate the solution yields coloured precipitates, some of which dissolve in potash, whilst the others are insoluble and have not yet been obtained pure. The hydrazine-derivative soluble in alkalis is recrystallised from benzene and afterwards from dilute alcohol. It then has a constant melting point.

The products of the oxidation of glycerol by platinum-black ferment in contact with beer yeast, and yield carbonic anhydride and ethyl alcohol. Fermentation is slow owing to the presence of a large quantity of unaltered glycerol, and is never complete.

The formation of hydrazine-derivatives soluble in alkalis, and the small quantity of carbonic anhydride evolved, compared with the reducing power of the product, indicate the formation of an aldehydic acid. Other oxidising agents, such as chromic acid, chlorine, bromine, or sunlight convert glycerol into substances having great reducing power.

Erythrol in contact with platinum-black is oxidised more slowly than glycerol, but seems to yield products which have a strong reducing power, and are fermented by yeast.

The author refers to a paper by Fisher and Tafel (this vol., p. 651) on azones derived from the products of oxidation of glycerol and erythrol. C. H. B.

Alkyl Hypochlorites from Isonitroso-compounds. By R. Möhlau and C. Hoffmann (*Ber.*, **20**, 1504—1507).—When an aqueous solution of hydroxylamine is treated with hypochlorous acid (equal mols.), a reaction takes place with formation of nitrogen, chlorine, and water.

Acetoxime hypochlorite, NOCl : CMe_2, is obtained by adding a solution of hypochlorous acid (prepared by saturating a cold 10 per cent. solution of soda) to a saturated aqueous solution of acetoxime kept cold with ice. An excess of hypochlorous acid must be used, and the whole well shaken until the blue colour at first produced disappears. The ether is then separated, washed with water, and dried with calcium chloride. It is a mobile liquid of an agreeable odour, sparingly soluble in water, readily in alcohol and ether. When cooled by means of ether and carbonic anhydride, it solidifies to colourless prisms. It distils with steam. When suddenly heated it explodes, but when carefully heated, boils at 134° (uncorr.) with partial decomposition.

Acetaldoxime hypochlorite, NOCl : CHMe, is prepared in a manner similar to the above compound. It is a colourless liquid having a powerful odour; it decomposes very readily, giving off hydrogen chloride, and could not be analysed. It explodes when heated.

N. H. M.

Capraldoxime and Methylhexylacetoxime. By A. Béhal (*Bull. Soc. Chim.*, **47**, 163—165).—The aldoxime and acetoxime were prepared from the capraldehyde and methyl hexyl ketone respectively, which were shown to be distinct compounds in a preceding memoir (this vol., p. 788). The compounds obtained are very similar to one another in appearance, being oleaginous liquids which do not yield

crystals when cooled with ice and salt; they have an aromatic odour and are lighter than water in which they are insoluble; they dissolve readily, however, in alcohol and ether. The aldoxime boils at 121° to 123°, and the acetoxime at from 116° to 117°. A. P.

Synthetic Acetic Acid and its Derivatives. By L. Henry (*Compt. rend.*, **104**, 1278—1281).—Synthetic acetic acid from acetonitrile has never been examined and compared with acetic acid produced in the ordinary way.

Acetonitrile was prepared by the action of methyl iodide on potassium cyanide, and was converted into acetic acid by mixing with 2·5 parts of hydrochloric acid of 40 per cent. in a well-cooled flask. When the reaction ceases the liquid is heated on a water-bath for several hours, the acid distilled off, converted into the anhydrous sodium salt, and decomposed by dry hydrogen chloride.

The acid thus obtained was carefully compared with acetic acid produced by fermentation and by the destructive distillation of wood. It was converted into monochloracetic acid, ethyl acetate, and acetamide, and a portion of the monochlor-derivative was converted into malonic acid by Kolbe and Muller's method.

Synthetic acetic acid and its derivatives are identical in every respect with the corresponding compounds prepared in the ordinary way, and hence they may be used in the preparation of the β, γ, and δ monosubstitution-derivatives of methane (this vol., p. 711).

C. H. B.

Cyanacetic Acid. By L. Henry (*Compt. rend.*, **104**, 1618—1621).—The hydrogen in the CH_2-group in malonitrile can be replaced by metals, notably by silver, and the hydrogen in hydrocyanic acid is distinctly basic. It was therefore to be expected that the hydrogen in the CH_2-group in cyanacetic acid, united as it is with a cyanogen-group and a carboxyl-group, would likewise be basic. Experiment confirms this conclusion.

A solution of ethyl cyanacetate in ether is rapidly and energetically decomposed by sodium, with evolution of hydrogen and separation of a white, pulverulent substance insoluble in ether. This product, *ethyl cyanosodacetate*, is a very light, very hygroscopic, and easily fusible solid, which reacts readily with haloïd ethers, forming liquids which have a more agreeable odour than that of cyanacetic acid, and are insoluble in, and heavier than, water. The following compounds were obtained in this way:—*Ethyl methylcyanacetate*, which boils at 194°, vapour-density 4·34; *ethyl ethylcyanacetate*, which boils at 204—205°; and *ethyl allylcyanacetate*, which boils at 215—220°

Ethyl cyanacetate is rapidly decomposed by aqueous ammonia, and if the solution is allowed to evaporate spontaneously, crystals of cyanacetamide separate. The alkyl-derivatives just described are only very slowly attacked by ammonia. *Cyanacetamide*, $CN{\cdot}CH_2{\cdot}CONH_2$, crystallises from alcohol in small needles, which melt at 118°; *ethylcyanacetamide*, $CN{\cdot}CHEt{\cdot}CONH_2$, forms small, nacreous plates which melt at 113°.

Ethyl cyanosodacetate readily reacts with carbonic chloride, yielding a crystalline product, $CN{\cdot}CH(COOEt)_2$.

The alkyl-derivatives are very readily obtained by Conrad and Limpach's method, that is, by the action of the corresponding alkyl-iodides on the product of the action of an alcoholic solution of sodium ethoxide on ethyl cyanacetate.

The hydrogen of the CH_2-group is very readily replaced by chlorine and bromine. The chlorine-derivative, CN·CHCl·COOEt, is a colourless liquid which has a pungent odour like that of chloropicrin, and boils at about 190°; vapour-density 5·11.

Pure cyanacetic acid is readily obtained in well-defined, white crystals which melt at 65—66°, and not at 55° as stated by Van t'Hoff. C. H. B.

Ethyl Cyanacetate. By A. Haller (*Compt. rend.*, **104**, 1626—1627).—When a solution of ethyl cyanacetate in its own volume of absolute alcohol is treated with the theoretical quantity of sodium ethoxide, it yields a crystalline magma of ethyl cyanosodacetate, CN·CHNa·COOEt, which is dried on porous plates and then over sulphuric acid in a vacuum. This compound forms white crystals almost insoluble in alcohol, but soluble in water, by which it is decomposed. When exposed to air it absorbs water and carbonic anhydride.

If the alcohol is present in sufficient quantity to keep the sodium-derivative in solution, the corresponding derivatives of the other metals can be obtained by double decomposition, but have not yet been analysed. The silver-derivative is yellow, but rapidly becomes brown when exposed to light, and black when boiled with water; the copper-derivative is greenish-blue, and becomes grey when heated with water; the zinc-derivative is white.

When an alcoholic solution of ethyl cyanosodacetate is treated with ethyl iodide, it yields a product which boils at 210—215°; with an ethereal solution of acetic chloride it yields ethyl cyanacetoacetate, identical with the product obtained by the author and Held by the action of cyanogen chloride on ethyl acetosodacetate. C. H. B.

α-Methylamidovaleric Acid. By A. Menozzi and C. Belloni (*Gazzetta*, **17**, 116—119).— *α-Methylamidovaleric acid*,

$$CH_2Me·CH_2·CH(NHMe)·COOH,$$

a homologue of sarcosine, is formed by warming a mixture of butaldehyde and hydrocyanic acid in molecular proportion, then adding the required quantity of methylamine; the nitrile thus obtained is then saponified. The acid crystallises in long, glistening needles very soluble in water; it sublimes slightly at 110°, more completely at 160°. The salts are very soluble in water and alcohol. The *nitrate* and *sulphate* crystallise in needles, the *sulphate* in prisms; the *copper* salt, $Cu(C_6H_{13}NO_2)_2,2H_2O$, in violet-blue prisms. V. H. V.

Substituted Crotonic Acids. By W. Autenrieth (*Ber.*, **20**, 1531—1533).—Escales and Baumann (Abstr., 1886, 879) obtained a thiophenylcrotonic acid melting at 176—177° from ethyl β-dithiophenylbutyrate. The same acid can be obtained from chlorcrotonic

acid, melting at 59°, by the action of sodium phenylmercaptide. The chlorocrotonic acid melting at 94° yields an isomeric thiophenylcrotonic acid which melts at 158° with evolution of carbonic anhydride. It is much more soluble in alcohol than the isomeride of higher melting point, and the barium salt crystallises with 1 mol. H_2O. The two thioethylcrotonic acids corresponding to the thiophenylcrotonic acids melt at 91—92° (from chlorocrotonic acid melting at 59°) and 113—115° respectively. N. H. M.

Croton Oil. By Kobert (*Chem. Zeit.*, **11**, 416).—Senier found that English pressed croton oil dissolved or was miscible with alcohol in any proportion not exceeding the volume of the oil employed, but that if an excess of alcohol was used, some of the oil was rendered insoluble. By this means he separated croton oil into two distinct parts possessing different physiological properties, the part soluble in alcohol possessing the well-known vesicating but no purgative property, whilst the insoluble portion was found to possess the purgative but not the vesicating property (Abstr., 1884, 909, 947).

This separation by means of alcohol, the present author contends, is incorrect. The chief element in the solubility is the age of the oil, and there are, moreover, some kinds of croton oil soluble in every proportion of alcohol.

He further states that the purgative and vesicating properties of croton oil are due solely to the presence of crotonolic acid which exists free and combined as a glyceride in all croton oils. A process is given for the preparation of the pure acid from croton oil.

J. P. L.

Acids from Drying Oils. By K. Hazura and A. Friedrich (*Monatsh. Chem.*, **8**, 156—164; compare this vol., p. 359).—When the acids from poppy and nut oils (30 grams) are saponified with 36 c.c. of a solution of potassium hydroxide (sp. gr. = 1·27), the product dissolved in 3 litres of water, and oxidised with a solution of potassium permanganate (30 grams) in water (3 litres), they both yield 4 to 5 grams of sativic acid, $C_{18}H_{32}O_2(OH)_4$, melting at 161—162°. When the two acids are treated with bromine they yield the same bromo-derivatives as does the acid from hemp oil: a compound melting at 175°, and the compound $C_{18}H_{32}Br_4O_2$ melting at 112—115°. Sativic acid is also formed when linoleic acid is oxidised in dilute solution; when a more concentrated solution is oxidised, sativic acid and *linusic acid*, $C_{18}H_{36}O_8$, are formed. The latter crystallises from water in microscopic needles melting at 203°; it is a monobasic acid. The *acetyl-derivative*, $C_{18}H_{30}O_2(OAc)_6$, is a thick, yellow oil. When linoleic acid in concentrated alkaline solution is oxidised with finely-powdered potassium permanganate, azelaïc acid, $C_9H_{16}O_4$, is formed. Bromine acts on linoleic acid with formation of a compound, $C_{18}H_{30}Br_6O_2$, identical with the tetrabromide of the dibromo-acid from hemp oil.

The authors think it probable that linoleic acid contains an unsaturated acid of the series $C_nH_{2n-6}O_2$, which yields linusic acid when oxidised. The presence of such an acid would also account for the fact that linoleic acid dries more readily than the others.

N. H. M.

Acid from Hemp-seed Oil. By K. Hazura (*Monatsh. Chem.*, **8**, 147—155).—The *tetrabromide* of the acid from hemp-seed oil, $C_{18}H_{32}Br_4O_2$, is formed together with the *tetrabromide of the dibromo-acid*, $C_{18}H_{30}Br_6O_2$, when 50 grams of the acid dissolved in glacial acetic acid is treated with 21 grams of bromine. It crystallises in white, lustrous plates which melt at 114—115°, and dissolve readily in glacial acetic acid, chloroform, benzene, ether, and alcohol; it is insoluble in water. The *salts*, with the exception of the alkali salts, are insoluble in water and in ether. The compound $C_{18}H_{30}Br_6O_2$ is white, melts at 177°, is very sparingly soluble in alcohol, glacial acetic acid, benzene, &c., insoluble in water. When the acid $C_{18}H_{32}Br_4O_2$ is reduced with tin and hydrochloric acid, the bromine is eliminated but not replaced by hydrogen. These results point to the formula $C_{18}H_{32}O_2$ for the acid from hemp oil. Sativic acid is shown to be *tetrahydroxystearic acid*, $C_{18}H_{32}O_2(OH)_4$. *Tetracetylsativic acid*, $C_{18}H_{32}O_2(OAc)_4$, prepared by boiling sativic acid with acetic anhydride, forms a light-yellow oil insoluble in water, soluble in alcohol, ether, light petroleum, &c.

N. H. M.

Ethyl Cyanacetoacetate. By A. Haller and A. Held (*Compt. rend.*, **104**, 1627—1629).—The ethyl cyanacetoacetate obtained by James (Trans., 1887, 287) by the action of potassium cyanide on ethyl chloracetoacetate is identical with the compound obtained by the authors (Abstr., 1882, 1280) by the action of cyanogen chloride on ethyl acetosodacetate. The formation of this compound from ethyl chloracetoacetate shows that the latter has the constitution

$$CHAcCl\cdot COOEt,$$

and not $CH_2Cl\cdot CO\cdot CH_2\cdot COOEt$, as supposed by James.

A much higher yield can be obtained by James's method than is stated in his paper.

C. H. B.

Preparation of Levulinic Acid. By P. Rischbieth (*Ber.*, **20**, 1773—1775).—The following method is recommended as avoiding the use of the large quantities of ether required in the usual process. 3 kilos. of powdered potato-starch are added to 3 litres of hydrochloric acid of sp. gr. 1·1, contained in a pan on the water-bath, the mixture being constantly stirred until all is dissolved to a thin syrup. This is then transferred to two capacious flasks provided with reflux tubes, and heated for 20 hours in a vigorously boiling water-bath. The magma obtained is pressed in order to separate humous substances, and the liquid is again heated for some hours on the water-bath in a flask connected to a water-pump, when water, hydrochloric acid, and formic acid distil. The residual syrup (consisting mainly of levulinic acid) is then transferred to a capacious fractioning flask, and heated in an oil-bath under reduced pressure, when nearly pure levulinic acid passes over at 135—150° under 60 mm. pressure. The distillate solidifies completely, either spontaneously or when a fragment of crystallised levulinic acid is added. The acid is further purified, with but slight loss, by redistillation in a vacuum. The yields is 13 to 14 per cent. of the starch employed.

A. J. G.

Salts of Lævulinic Acid. By J. Block and B. Tollens (*Annalen*, **238**, 301—302).—*Barium lævulinate*, $(C_5H_7O_3)_2Ba + 2H_2O$, is slowly deposited from concentrated solutions in needle-shaped crystals, freely soluble in water. *Strontium lævulinate*, $(C_5H_7O_3)_2Sr + 2H_2O$, crystallises in prisms. It is also freely soluble in water. W. C. W.

Propylxanthic Acid. By A. Scala (*Gazzetta*, **17**, 78—82).—*Potassium propyl xanthate*, SK·CS·OPr, crystallises in yellow, silky needles, very soluble in water, sparingly soluble in alcohol and ether. Its *copper* salt is an orange-yellow, the *silver* salt a pale yellow, the *lead* and *mercury* salts white precipitates. On adding hydrochloric acid to a solution of the potassium salt, the free acid separates as a pale yellow, insoluble oil, rapidly decomposing into its constituents. *Propyldioxythiocarbonate*, OPr·CS·S_2·CS·OPr, prepared from iodine and potassium propyl xanthate, is a pale yellow oil of peculiar odour. With alcoholic ammonia it yields a crystalline precipitate, probably the amide of the acid. *Methyl propyl xanthate*, SMe·CS·OPr, is a pale yellow oil of a nauseous, garlic-like odour, boiling at 202—203·5°; the *ethyl* salt, of similar appearance and odour even more disagreeable, boils at 215·6—217·6°. Determinations of the vapour-densities of these compounds are given. V. H. V.

Potassium Manganic Oxalate. By F. Kehrmann (*Ber.*, **20**, 1594—1596).—*Potassium manganic oxalate*, $K_6Mn_2(C_2O_4)_6 + 6H_2O$, is always obtained as an intermediate product when solutions of potassium permanganate are reduced with oxalic acid in the cold, but in the presence of an excess of oxalic acid the reduction goes further, and the method is unsuitable for the isolation of the compound. It can, however, be separated if the calculated quantities of finely powdered hydrogen potassium oxalate and oxalic acid are gradually added to a mixture of manganic hydroxide and snow or finely powdered ice, and the deep purple-red solution, after rapid filtration, is mixed with alcohol until crystallisation commences, and then allowed to remain for 1 to 2 hours in a mixture of ice and salt. It crystallises in almost black, monoclinic prisms, transmitting light of a red colour at the edges, and is isomorphous with the corresponding iron salt; the two compounds show the same habitus, and when mixed in suitable proportions give mixed crystals on the addition of alcohol to the saturated aqueous solution. The salt is tolerably stable at the ordinary temperature and in the absence of light, but sunlight and heat decompose it with the evolution of carbonic anhydride. In water just slightly warm the salt dissolves at first without alteration, but soon decomposes with the evolution of much carbonic anhydride. The *barium* salt is obtained in dark red, sparingly soluble scales on the addition of barium chloride to a cold solution of the potassium salt. W. P. W.

Addition of Ethyl Malonate to Compounds containing Doubly-linked Carbon-atoms. By L. Claisen (*J. pr. Chem.* [2], **35**, 413—415.)—A. Michael has described as a new reaction the addition of ethyl malonate or ethyl acetoacetate to substances with

doubly-linked carbon-atoms (this vol., p. 672). It is pointed out that the action of the aldehydes on ethyl malonate and ethyl acetoacetate, described by Komnenos and Claisen, Perkin, Junr., and by Hantzsch, is exactly similar, the first product of the action being a non-saturated compound, which then again enters into reaction exactly as described by Michael (compare Abstr., 1884, 422, 443, 444, 445). H. B.

α-Amidoisosuccinic Acid. By G. Koerner and A. Menozzi (*Gazzetta*, **17**, 104—109).—*α-Amidoisosuccinic* or *α-isoaspartic acid*, $NH_2 \cdot CMe(COOH)_2$, is formed on warming a mixture of pyruvic and hydrocyanic acids under pressure; the product is treated with alcoholic ammonia, the nitrite formed is best saponified by barium hydrate, and the barium salt decomposed by sulphuric acid. The free acid crystallises in transparent prisms, readily decomposed, when heated at 100°, into α-alanine and carbonic anhydride. In conformity with the hypothesis of Van t'Hoff, the acid is optically inactive. The salts of the alkali and alkaline earth metals crystallise in needles, soluble in cold, more so in hot water; the copper salt forms sparingly soluble, blue needles, and the silver salt a white, flocculent precipitate. The hydrochloride, sulphate, and nitrate crystallise in transparent prisms.

V. H. V.

Butyl Sebacate. By G. Gehring (*Compt. rend.*, **104**, 1289—1290). Butyl sebacate is obtained by the action of hydrogen chloride on a mixture of normal butyl alcohol and sebacic acid heated at 150°. It is a colourless liquid, with an agreeable, aromatic odour and a burning taste. It is insoluble in water; is miscible with alcohol in all proportions, and somewhat less miscible with ether; sp. gr. at 0° = 0·9417; at 15° = 0·9329. It boils at 344—345° without decomposition. Small quantities on a glass rod burn with a flame with a deep blue centre, but the liquid cannot be ignited on the surface by a Bunsen burner.

Butyl sebacate is decomposed by sulphuric acid in the cold, with evolution of sulphurous anhydride. With ammonia it yields white microscopic needles of sebacamide, $C_8H_{10}(CONH_2)_2$, and when treated with chlorine in sunlight a solid is formed, which is probably $C_{10}H_{16}O_4(C_4Cl_9)_2$. C. H. B.

Perchloramyl Perchlorosebacate and Perchlorobutyl Perchlorosebacate. By G. Gehring (*Compt. rend.*, **104**, 1624—1625).—When dry chlorine is passed into a flask containing isoamyl sebacate exposed to sunlight, the chlorine is somewhat rapidly absorbed with considerable development of heat. When the energy of the reaction diminishes the flask is gradually heated, the temperature being eventually raised to 230°. The substance becomes solid, but continues to absorb chlorine, and again becomes liquid. After about four days, long, white needles separate, and these are removed from time to time and dried over lime and sulphuric acid in a vacuum. They are purified by sublimation and washing with water and alcohol. The compound thus obtained is *perchloramyl perchlorsebacate*, $(C_5Cl_{11})_2C_{10}Cl_{16}O_4$. It forms long, semitransparent, rhombic prisms, which melt at 179°, sublime readily, and when exposed to moist air become yellow,

resinous, and acid, and eventually volatilise. It has an aromatic smell, but no taste, is of a waxy consistency and cannot be powdered. It is heavier than water, and is volatile in water vapour. It will not dissolve in water, but is slightly soluble in alcohol and very soluble in ether, chloroform, benzene, light petroleum, and terebenthene.

Perchlorobutyl perchlorosebacate, $(C_4Cl_9)_2C_{10}Cl_{16}O_4$, is obtained in a similar manner, but the action is still more rapid. It forms snow-white, hexagonal prisms, which melt at 172° and boil at 200°. Its other properties resemble those of the preceding compound, but after washing with much water it becomes hard and brittle.

C. H. B.

Reciprocal Transformation of the Optically Active Asparagines. By A. Piutti (*Gazzetta*, **17**, 126—128).—The inactive aspartic acid, when converted into the ethereal salt, and then heated with alcoholic ammonia, yields a crystalline mixture of the optically active asparagines. The transformation is somewhat similar to that effected by Jungfleisch in the case of tartaric acid. The monethyl aspartate is best obtained by decomposing the copper salt with hydrogen sulphide; it crystallises in micaceous laminæ, melting at 200° with decomposition.

V. H. V.

Alkyl-compounds of Bismuth. By A. Marquardt (*Ber.*, **20**, 1516—1523. Compare Michaelis and Michaelis and Polis, this vol., p. 368).—These compounds are prepared by adding an ethereal solution of bismuth bromide (2 mols.) to a solution of zinc alkyl in ether. The ether is afterwards distilled off in a current of carbonic anhydride, and the residue treated with aqueous soda in an atmosphere of hydrogen when the bismuth alkyl separates.

Trimethylbismuthine, $BiMe_3$, is a clear, mobile, strongly refractive liquid, having a very disagreeable, irritating odour, sp. gr. = 2·30 at 18°. It fumes in air but does not inflame. It boils at 110°, dissolves readily in ether, alcohol, glacial acetic acid, and light petroleum; it is insoluble in water. When heated in air it explodes violently. It distils readily with steam, but decomposes when long in contact with water. Strong hydrochloric acid decomposes it with formation of bismuth chloride and methane.

Dimethylbismuthine chloride, $BiMe_2Cl$, separates in flakes when chlorine is passed through a solution of trimethylbismuthine in light petroleum, kept cold by means of ice and salt, and is purified by washing with a mixture of alcohol and much ether. It melts at 116° and dissolves readily in alcohol; it is insoluble in ether.

Dimethylbismuthine bromide, $BiMe_2Br$, forms a white powder, readily soluble in alcohol, insoluble in ether. It inflames when warmed.

Methylbismuthine dichloride, $BiMeCl_2$, is obtained by the action of trimethylbismuthine on bismuth chloride dissolved in glacial acetic acid. It separates in yellowish-white plates, melts at 242°, and dissolves sparingly in alcohol and glacial acetic acid, and is insoluble in ether.

Methylbismuthine dibromide, $BiMeBr_2$, forms a yellow powder melting at 214°; it is insoluble in ether, sparingly soluble in alcohol, benzene, &c. The *diiodide*, $BiMeI_2$, is prepared by heating methyl

iodide and trimethylbismuthine at 200°, and forms lustrous, brick-red crystals, rather readily soluble in alcohol. It becomes black when exposed to light, and melts at 225° with decomposition.

Diethylbismuthine bromide, $BiEt_2Br$, is a powder; it inflames in air. The chloride, $BiEtCl_2$ (Dünhaupt, *Annalen*, **92**, 371), and the *bromide*, $BiEtBr_2$, were prepared in like manner to the methyl-compounds. The *iodide*, $BiEtI_2$, forms lustrous, bright-red crystals.

Methylbismuthine oxide, BiMeO, is obtained by treating with ammonia the zinco-bromide of bismuth methyl bromide dissolved in alcohol. It inflames when warmed, dissolves readily in aqueous soda, and is insoluble in water.

Dimethylbismuthine hydroxide, $BiMe_2{\cdot}OH$, is formed when bismuth methyl bromide is treated with water. It is inflammable. Water decomposes it slowly. When heated with methyl iodide at 100°, bismuth monomethyl iodide is formed. N. H. M.

Furfuran-derivatives. By G. Nuth (*Ber.*, **20**, 1332—1338).—Hantzsch described (Abstr., 1886, 707) the formation of complex furfuran-derivatives by the action of sodium phenoxides on ethyl chloracetoacetate, and of sulphuric acid on the resulting compound. The author has employed substituted phenols in analogous reactions.

Ethyl paranitromethylcumarilate, $NO_2{\cdot}C_6H_3{<}\overset{O\,\text{—}}{CMe}{>}C{\cdot}COOEt$, formed from paranitrophenol and ethyl chloracetoacetate, crystallises in white needles, is soluble in ether and the usual solvents, and melts at 74°. The free *acid* forms yellow needles, moderately soluble in boiling water, ether, and alcohol; it melts at 178°. Its salts are sparingly soluble; the lead, mercury, cobalt, copper, and silver salts were prepared. The above reaction only took place when the constituents were heated together in an anhydrous condition. Metanitrophenol appears to act in a similar way, but the yield was very small. The ortho-compound gave very unsatisfactory results. Methyl salicylate yielded no furfuran-derivative.

Quinol yielded *ethyl parabenzodimethyldifurfurandicarboxylate*, $C_6H_2\left(\overset{O\,\text{—}}{CMe}{>}C{\cdot}COOEt\right)_2$. This substance crystallises in greenish, glistening scales, very sparingly soluble in the usual solvents, insoluble in cold alkalis; it melts at 150°. The free *acid* forms a yellowish-green, amorphous mass containing 1 mol. H_2O, which it loses at 110°. The alkaline salts are soluble, the remainder insoluble. When distilled with lime, the potash salt yields *parabenzodimethyldifurfuran*, $C_6H_2\left(\overset{O\,\text{—}}{CMe}{>}CH\right)_2$. This crystallises in large, glistening tables, having a bluish fluorescence. It is soluble in alcohol, ether, &c., and melts at 108°.

Quinol yields only the above difurfuran-derivative. When the monosodium-compound of quinol is used instead of the di-compound the result is a diminished yield, but no monofurfuran-derivative is formed.

Catechol likewise yields only *ethyl orthobenzodimethyldifurfurandicarboxylate*. This crystallises in short, white prisms and melts at

155°. The free *acid* resembles that of the para-compound, but contains no combined water.

The para-compounds when warmed with strong sulphuric acid give the intense blue coloration characteristic of most furfuran-derivatives, but the ortho-compounds give a green coloration which, on stronger heating, changes to steel-blue.

The difurfuran obtained by Hantzsch from resorcinol (this vol., p. 262) melts at 27° and not at 17° as originally given. L. T. T.

Normal Propylthiophen-derivatives: Glyoxylic Acids of the Thiophen Series. By H. Ruffi (*Ber.*, **20**, 1740—1750).—It was thought that it might be possible to oxidise propylthiophen into an acid of the formula $C_4SH_3{\cdot}CO{\cdot}CO{\cdot}COOH$, but notwithstanding many variations in the method of working, α-thiophenic acid was always obtained.

Bromopropylthiophen, $C_4SH_2BrPr^{\alpha}$, prepared by shaking propylthiophen with bromine-water (equimolecular proportions), is a colourless oil of aromatic odour and boils at 189°. The *dibromo*-compound, $C_4SHBr_2Pr^{\alpha}$, is prepared in a similar manner; it is a clear yellow oil of agreeable odour and boils at 248°. A tribromo-derivative seemed also to be formed in small quantity at the same time, but attempts to prepare it by treating dibromopropylthiophen with pure bromine led to the formation of tetrabromothiophen. *Iodopropylthiophen*, $C_4SH_2IPr^{\alpha}$, was also prepared; it is a yellow oil of agreeable odour which volatilises with steam, but cannot be distilled alone. *Dinitropropylthiophen*, $C_4SH(NO_2)_2Pr^{\alpha}$, is prepared by drawing the vapours of propylthiophen through fuming nitric acid; it is a yellow oil and can be distilled with steam.

Propylthiophenic acid, $C_4SH_2Pr^{\alpha}{\cdot}COOH$, is obtained as its ethyl salt by heating a mixture of iodopropylthiophen (20 grams), ethyl chlorocarbonate (10 grams), and 1 per cent. sodium amalgam (500 grams), and distilling the product with steam, when the ethyl salt passes over as an oil. The free acid crystallises in slender needles or lamellæ and melts at 57° (uncorr.).

Acetopropylthiënone, $C_4H_2SPr^{\alpha}{\cdot}COMe$, is prepared by heating propylthiophen dissolved in light petroleum with acetic chloride and aluminium chloride. It is a yellow oil of fruity odour and boils at 255° (uncorr.). The *phenylhydrazide* is crystalline and melts at 60°. The *oxime*, $C_4SH_2Pr^{\alpha}{\cdot}CMe:NOH$, crystallises in slender needles and melts at 55°.

Propylthiënylglyoxylic acid, $C_4SH_2Pr^{\alpha}{\cdot}CO{\cdot}COOH$, is obtained by oxidising acetopropylthiënone with an alkaline solution of potassium permanganate at the ordinary temperature, as an oil which gradually crystallises.

α-α-Methylthiënylglyoxylic acid, $C_4SH_2Me{\cdot}CO{\cdot}COOH$ [= 2 : 5], is prepared by acetylising α-thiotolen (obtained from levulinic acid) and oxidising the ketone so obtained. It melts at 80°. The calcium and barium salts were prepared.

α-β-Methylthiënylglyoxylic acid, [= 3 : 5 ?], is prepared in like manner from β-thiotolen (from pyrotartaric acid). It crystallises in long needles, melts at 142° and sublimes, even at the ordinary tempera-

ture. When heated with hydroxylamine and aqueous potash it yields a nitroso-acid, $C_4SH_2Me{\cdot}C(NOH){\cdot}COOH$, which crystallises in colourless needles and melts at 104°. The phenylhydrazide melts at 141°. The acid does not react with bromine.

α-α-Dimethylthiënylglyoxylic acid, $C_4SHMe_2{\cdot}CO{\cdot}COOH$ [= 2 : 5 : 3], is formed, together with an acid melting at 106°, by oxidising acetothioxylen (Messenger, Abstr., 1885, 1205). It is obtained as an oil which gradually solidifies.

From these results it follows that the acetylised thiophens when oxidised first yield glyoxylic acid, and this, whether or no the carbon-atom to which the acetyl-group is attached is in direct union with the sulphur-atom. A. J. G.

Bye-products of the Manufacture of Thiophen. By V. Meyer and K. Neure (*Ber.*, **20**, 1756).—The material worked on was an oil boiling above 220° obtained in the manufacture of thiophen by distilling succinic acid with phosphorous sulphide. When exposed to cold, the greater part crystallised; the crystals proved to be thiosuccinic anhydride. Small quantities of succinic anhydride were also obtained. The liquid portion when distilled with steam, gave a distillate heavier than water, most of which was soluble in alkalis. The insoluble portion was too small for proper investigation; it probably contained the still unknown thiënyl sulphide. The substance soluble in alkali proved to be thiënyl mercaptan, and as a considerable amount was obtained further investigation of its derivatives was made.

The *acetate*, $C_4SH_3{\cdot}SAc$, is a colourless oil boiling at 230—232°. *Thiënyl disulphide*, $S_2(C_4SH_3)_2$, obtained by the spontaneous evaporation in contact with air of a solution of the mercaptan in concentrated alcoholic ammonia, crystallises in yellow, lustrous needles and melts at 55—56°. The *silver* salt, $C_4SH_3{\cdot}SAg$, is obtained as a yellow precipitate on adding silver nitrate to a neutralised solution of the mercaptan. *Methyl thiënyl thioether*, $C_4SH_3{\cdot}SMe$, is obtained by the action of sodium hydroxide and methyl iodide on the mercaptan; it is a colourless oil and boils at 186°.

If thiënyl mercaptan is mixed with powdered diazobenzenesulphonic acid and a little water added, the liquid boils with vigorous evolution of gas, and an oil soluble in ether is formed. This reaction, which differs very essentially from that of phenyl mercaptan, could not be further studied from want of material. A. J. G.

Formation of Croconic Acid from Benzene-derivatives. By R. Nietzki (*Ber.*, **20**, 1617—1620).—When aqueous potash or soda is added to a solution of an alkaline salt of rhodizonic acid, the intense reddish-yellow colour changes to a pale-yellow and is not restored on neutralisation with an acid, whilst the resulting solution on acidification with acetic acid and treatment with barium chloride remains clear, and only begins to deposit the yellow barium croconate after remaining for one day. The intermediate compound thus evidently formed during the conversion of rhodizonic into croconic acid is obtained as a flocculent, orange-yellow barium salt on addition of ammonia to the acetic acid solution after treatment with barium

chloride, and the yield is equally good whether the operation is conducted in air or hydrogen. The new barium salt is identical with the barium salt of croconic acid hydride (Abstr., 1886, 449), but on analysis gives figures which agree better with the formula $C_5H_2O_5Ba + 2H_2O$ than that previously assigned to the compound. Croconic acid hydride, $C_5H_4O_5$, most probably has the formula

$$<\begin{matrix}CO\cdot C(OH)\\CO\cdot C(OH)\end{matrix}>CH(OH),$$

and adopting the suggestion thrown out by Zincke (*Ber.*, **20**, 1267, footnote), the author considers that rhodizonic acid first yields a labile hydroxy-acid, $<\begin{matrix}CO\cdot C(OH)\\CO\cdot C(OH)\end{matrix}>C(OH)\cdot COOH$, which at once breaks up into carbonic anhydride and croconic acid hydride.

W. P. W.

The Halogen Carriers in the Natural Groups of the Elements. By C. Willgerodt (*J. pr. Chem.* [2], **35**, 391—400).—Benzene was treated with chlorine in the dark and in presence of the various substances examined, the alteration in weight noticed, and the product then subjected to fractional distillation. Yttrium and yttrium chloride are without action, lanthanum has a slight action; titanium none, germanium and germanium chloride none; zirconium is very active, and is thus the first active element in the carbon-group; cerium and cerium chloride are inactive, thorium and thorium chloride are almost inactive. Vanadium oxychloride, $VOCl_2$, acts slightly; niobium and niobium chloride are active, didymium chloride is inactive, but tantalum and tantalum chloride are active. Of the elements of the oxygen-group, molybdenum and tellurium have already been shown to be very active; chromic chloride is inactive, and it therefore appears unlikely that sulphur is a chlorine carrier as has been stated previously by the author, and he now shows that the monochloride is quite inactive; uranium and uranium tetrachloride are active, the latter especially so. In the fluorine-group the only known chlorine carrier is iodine. H. B.

The Halogen-benzene Haloïds: α-Trichlorobenzenehexachloride. By C. Willgerodt (*J. pr. Chem.* [2], **35**, 415—416).—Reference is made to previous work and to further experiments on paradichlorobenzenehexachloride. α-Trichlorobenzenehexachloride, $C_6H_3Cl_3,Cl_6$ [$Cl_3 = 1:2:4$], is crystalline, melts at 95—96°, and when heated with alcoholic potash yields pure hexachlorobenzene. H. B.

Action of Acetylene on Benzene in presence of Aluminium Chloride. By R. Varet and G. Vienne (*Compt. rend.*, **104**, 1375—1377).—A mixture of benzene (200 grams) and aluminium chloride (50 grams) was treated with a current of acetylene for five hours per day during six days. At the beginning of each treatment, the liquid was gently heated, but afterwards the heat developed by the reaction itself was sufficient. The product was washed with water and alkalis, and then fractionated. It consisted of 80 parts of cinnamene, boiling at 143—145°, 15 parts of diphenylethane boiling at 265—270°, and 5 parts of dibenzyl boiling at 280—286°.

No naphthalene hydride, $C_{10}H_{10}$, nor hydrocarbon, $C_{12}H_{12}$, was formed. C. H. B.

Influence of Light on the Action of Halogens on Aromatic Compounds. By J. Schramm (*Monatsh. Chem.*, **8**, 101—106).—Chlorine acts quickly on ethylbenzene in sunlight, with rise of temperature and formation of chlorethylbenzene; if sunlight is cut off by clouds or if the chlorine is passed in too quickly, substitution takes place in the benzene nucleus. The constitution of the product was determined by the method employed by Radziszewski for determining the constitution of α-bromethylbenzene. No other product is formed.

The action of chlorine on boiling ethylbenzene is much slower than in sunlight. The product contains the same chlorethylbenzene as that formed when the reaction takes place in sunlight (compare Abstr., 1886, 451). N. H. M.

Phenol. By E. Mylius (*Arch. Pharm.* [3], **25**, 308).—Various reasons have been assigned for the red colour of phenol; the author attributes it to the action of the alkali obtained from the glass containing vessel. He has previously pointed out the great difference in the solubility of various glasses, and the resulting precipitates induced in morphine and antimony solutions, &c. This is quite sufficient to account for the coloration (that is, the oxidation of phenol). Of course this is not sufficient to account for the colour where the phenol is red under all circumstances, but only when one and the same sample becomes red in one flask and not in another.

J. T.

Action of Sulphur Dichloride on Phenol. By G. Tassinari (*Gazzetta*, **17**, 83—87 and 90—94).—A violent reaction takes place on mixing sulphur dichloride and phenol; if this be moderated by lowering the temperature, a yellow solid gradually separates, which can be purified by solution in alkali and reprecipitation by carbonic anhydride. The compound, *hydroxyphenyl sulphide*, $S(C_6H_4{\cdot}OH)_2$, crystallises in leaflets, melting at 150°, sparingly soluble in cold, more readily in hot water. The reaction leading to its formation is as follows:—$2C_6H_5{\cdot}OH + SCl_2 = S(C_6H_4{\cdot}OH)_2 + 2HCl$; it is, however, probable that the phenolic hydrogen is at first displaced by the sulphur, and subsequently by an intramolecular change; the sulphur-atom displaces hydrogen in the phenyl-group. The metallic derivatives are unstable, but the acetyl-derivative, $(C_6H_4{\cdot}OAc)_2S$, is a sparingly soluble, crystalline substance, melting at 92—94°, partially decomposed on boiling with water, readily by alkalis.

In like manner parabromophenol yields a corresponding bromo-derivative, $S(C_6H_3Br{\cdot}OH)_2$, melting at 175—176°, converted by hydrogenation with zinc-dust into a hydroxyphenyl sulphide, crystallising in micaceous scales, isomeric with the compound above described. It melts at 128—129°, is very soluble in caustic potash, and gives a blue coloration with ferric chloride.

The homologues of phenol yield similar derivatives; in the paper are described *paramethylhydroxyphenyl sulphide*, melting at 117—

118°, the corresponding ortho-derivative, melting at 123—124°, *paramethylpropylhydroxyphenyl sulphide*, melting at 152—153°, and *hydroxynaphthoyl sulphide*, melting at 214—215°, probably identical with a compound obtained by Merz and Weith directly from β-naphthol. V. H. V.

Derivatives of Orthobenzoquinone. By T. Zincke (*Ber.*, **20**, 1776—1777).—Notwithstanding numerous attempts, orthobenzoquinone has never been prepared; the author, however, has now succeeded in obtaining its tetrabromo- and tetrachloro-derivatives by oxidising the corresponding catechol compounds.

Tetrabromorthoquinone, $C_6Br_4O_2$, is best obtained by dissolving tetrabromocatechol in hot glacial acetic acid, allowing to cool somewhat, and adding excess of nitric acid (sp. gr. 1·4) previously diluted with glacial acetic acid. The liquid turns deep red; it is allowed to remain for a few minutes, and the quinone then precipitated by the careful addition of water. The oxidation may also be effected with chlorine or bromine, but the result is far less certain than with nitric acid; finally the substance can be obtained directly from catechol by adding bromine to a hot solution of catechol in glacial acetic acid. It crystallises in thick, dark garnet-red prisms and tables, or, by quick cooling, in dark red, transparent plates of metallic lustre, melts at 150—151°, and is readily soluble in ether, alcohol, benzene, and glacial acetic acid, sparingly soluble in light petroleum. It is characterised by its oxidising powers; thus it oxidises quinol to quinone or quinhydrone, and dimethylaniline and methyldiphenylamine to blue colouring matters, being at the same time itself reduced to tetrabromocatechol. With aniline it yields a compound crystallising in bluish-black plates or thick needles, and melting at 172—173°; this compound would seem, however, to contain several aniline residues, and may, therefore, probably be a derivative of ordinary quinone.

The substance described by Stenhouse as erythrobromocatechol is considered by the author to be impure tetrabromorthoquinone.

A quinhydrone-like substance is obtained by mixing equal parts of tetrabromorthoquinone and tetrabromocatechol dissolved in ether or benzene, and separates on evaporation in black, lustrous needles, which melt with change of colour at about 110°.

Tetrachlororthoquinone, $C_6Cl_4O_2$, is prepared by the action of nitric acid on tetrachlorocatechol or directly by the action of chlorine on catechol. It is more difficult to prepare than the bromo-compound, which it resembles in appearance and reactions; it is, however, more soluble in glacial acetic acid, and melts at 131—132°.

Tetrachlorocatechol is obtained by passing chlorine into a hot concentrated solution of catechol in glacial acetic acid; it crystallises in colourless needles or thick plates, and melts at 174°. Tetrabromocatechol melts at 192—193°, not 187° as stated by Stenhouse.

A. J. G.

Dinitroso-orcinol and Dinitrosoresorcinol. By H. Goldschmidt and J. Strauss (*Ber.*, **20**, 1607—1611).—The behaviour of dinitroso-orcinol towards hydroxylamine should afford evidence as to whether it is a nitroso- or an isonitroso-derivative, since it is to be

supposed that in the latter case it would readily exchange the two atoms of oxygen present in the ketonic condition for two isonitroso-groups. 2 grams of the compound were heated at 100° with 15 grams of alcohol and 2 grams of solid hydroxylamine hydrochloride; after some time complete solution took place, and on further heating *toludiquinoyltetroxime*, $C_6HMe(NOH)_4$, separated as a yellow compound, indistinguishable in appearance from dinitroso-orcinol, and very sparingly soluble in all ordinary solvents. When this is heated with acetic anhydride, and the resulting solution poured into aqueous soda, the *anhydride*, $O<^{N}_{N}>C_6HMe<^{N}_{N}>O$, is obtained as an oil which crystallises from benzene in flat, white needles melting at 47°. Toludiquinoyltetroxime, dissolved in aqueous potash, and treated with a hot solution of potassium ferricyanide, yields the oxidation-product, $<^{NO}_{NO}>C_6HMe<^{NO}_{NO}>$ (comp. Koreff, Abstr., 1886, 363; Ilinski, *ibid.*, 472); this crystallises from benzene in pale yellow, thin, transparent needles, melts at 103°, and when moist becomes coloured red on exposure to the air.

Dinitrosoresorcinol, when similarly treated with hydroxylamine hydrochloride, yielded a compound richer in nitrogen; it could not, however, be obtained pure, but when heated with acetic anhydride was converted into the *anhydride* of diquinoyltetroxime, $C_6H_2N_4O_2$. This crystallises in white needles, melts at 61°, and is soluble in benzene and ether.

Dinitrosoresorcinol may therefore be regarded as diquinoyldioxime, $C_6H_2O_2(NOH)_2$ [NOH : O = 1 : 2 and 5 : 4], and dinitrosorcinol as toludiquinoyldioxime, $C_6HMeO_2(NOH)_2$ [NOH : O : Me : O : NOH = 1 : 2 : 3 : 4 : 5]. W. P. W.

Action of Acetaldehyde on Polyvalent Phenols. By H. Causse (*J. Pharm.* [5], **15**, 554—556).—The publication of a memoir by Claus and Trainer on the action of acetaldehyde on some monatomic phenols has led the author to publish a *résumé* of his researches on the aromatic acetals. In the action of acetaldehyde on some polyvalent phenols, the products obtained differ completely according to the method of preparation. Taking pyrogallol for example, 10 parts dissolved in 100 parts of water was mixed with 2 grams of sulphuric acid and heated at 60°, dilute aldehyde was then dropped in. The liquid became brown but nothing definite separated out. On removing from the water-bath, the temperature dropped, the liquid became troubled, the temperature rose, and the vessel became filled with a brown spongy mass. In this same liquid, maintained at 60°, if sulphuric acid is added in 5 c.c. portions up to one-tenth, and better, a solution made up of sulphuric acid 1 part, sodium sulphate 1 part, water 9 parts, the reaction is quite different, instead of a resinous body, beautiful crystals are obtained. These facts apply to catechol as well as to resorcinol, and the products obtained are clearly crystalline. The nature of the product depends moreover on the temperature. To 10 parts of hydrogen potassium sulphate dissolved in 100 parts of water is added 10 grams of resorcinol and 15 c.c. of pure aldehyde of

one-fifth. The flask is stoppered and heated at 20°. Crystals soon form and rapidly increase in volume. The liquid filtered from the colourless crystals and heated at 60° gives large, yellow crystals. The colourless crystals have a composition approaching to acetal sesquihydrate. The slight deviation in composition is due to the facility with which the hydrate parts with water of crystallisation. Exposed to the air it gradually becomes yellow; the same transformation is more readily effected by the action of anhydrous solvents. Thus anhydrous ether dissolves the colourless crystals, and deposits voluminous, anhydrous, yellow crystals which the author has described as resorcinol-acetal. The latter can exist in two forms—the one hydrated and colourless, the other yellow and anhydrous. J. T.

Formation of Haloïd Substitution-derivatives of Amido-compounds by the Reduction of Nitro-derivatives of Hydrocarbons. By E. Kock (*Ber.*, **20**, 1567—1569).—Some time ago the author observed that the reduction of metanitrotoluene with zinc-dust and hydrochloric acid results not only in the formation of metatoluidine but also of a solid compound which on examination is found to be identical with the chlorotoluidine (m. p. = 83°) described by Goldschmidt and Hönig (this vol., p. 363). An examination of the action of various reducing agents on other nitro-derivatives, under conditions as similar as possible with respect to temperature and concentration of the acid, has led to the results summarised in the table (p. 811).

The yield of the chlorinated amine is considerable; for example, from 70 grams of nitrobenzene, 29 grams of aniline and 17·5 grams of pure parachloraniline were obtained. The temperature during the reduction is found to exercise an essential influence on the yield of the chlorinated derivative.

The following derivatives of the chlorotoluidine (m. p. = 83°) are described:—The *sulphate*, $(C_6H_3MeCl\cdot NH_2)_2,H_2SO_4$, sparingly soluble in water; *diorthochlorometatolylcarbamide*, $CO(NH\cdot C_6H_3MeCl)_2$, crystallising in small scales melting at 271°; and the *thiocarbamide*, $CS(NH\cdot C_6H_3MeCl)_2$, crystallising in small, silky needles melting at 177°. W. P. W.

Metanitroparachloraniline. By A. Claus and A. Stiebel (*Ber.*, **20**, 1379—1382).—When orthoparadinitrochlorobenzene is dissolved in alcohol, concentrated hydrochloric acid added, and then just sufficient stannous chloride to reduce one nitro-group, the principal product is metanitro-orthochloraniline, which separates on the addition of water. If the mother-liquor is neutralised with ammonia a small quantity of *metanitroparachloraniline* is precipitated. This compound is also formed by nitrating parachloraniline dissolved in a large excess of strong sulphuric acid. It is soluble in alcohol, ether, chloroform, and boiling water; crystallises in long needles, and melts at 102·5—103° (uncorr.). It is more basic than the above orthochloro-derivatives, but its salts are decomposed by water. The *platinochloride* forms red crystals which decompose at 270°. The *acetyl-derivative* forms yellow needles melting at 99—100°. The con-

	Nitro-benzene	Liquid nitrotoluene (ortho- and para-)	Metanitro-toluene	Paranitro-toluene	α-Nitro-naphthalene	Orthonitro-phenol	Paranitro-phenol.	Meta-nitranisoïl.
Zinc-dust and hydrochloric acid	Aniline and parachlor-aniline	—	Meta-toluidine and orthochloro-metatoluidine	Chlorinated toluidine	Chlorinated naphthyl-amine	Pure orth-amidophenol	Pure par-amidophenol	Pure met-anisidine.
Zinc turnings and hydrochloric acid	*Ibid.*	Chlorinated toluidine	—	*Ibid.*	—	—	—	—
Iron filings and hydrochloric acid	Pure aniline	—	—	Pure para-toluidine	—	—	—	—
Stannous chloride in hydrochloric acid solution	*Ibid.*	—	Pure meta-toluidine	—	—	*Ibid.*	—	—

stitution was proved by replacing the amido-group by hydrogen and also by chlorine. The authors intend to make use of this compound in the synthesis of quinoline-derivatives. L. T. T.

Boiling Points of Diphenylamine and its Homologues. By C. Graebe (*Annalen*, **238**, 362—363).—The author has carefully redetermined the boiling points of the homologues of diphenylamine, and obtained the following results :—

	Bar. 727·5 mm.	Bar. 760 mm.
Diphenylamine	300°	302°
Phenylorthotoluidine	305	—
Diorthotolylamine	312	—
Phenylparatoluidine	317—315°	—
Diparatolylamine.....	328·5°	330·5

W. C. W.

Dibenzylaniline and its Derivatives. By C. Matzudaira (*Ber.*, **20**, 1611—1617).—*Dibenzylaniline*, $PhN(C_7H_7)_2$, is prepared by heating a mixture of benzyl chloride (15 parts), aniline (5·4 parts), and sodium hydroxide (3 parts) at 100° for about three weeks until a sample ceases to give the green colour of nitrosodibenzylamine when treated with hydrochloric acid and sodium nitrite. It crystallises in colourless needles, melts at 67°, and is readily soluble in ether and benzene, sparingly soluble in cold alcohol and acetic acid, and insoluble in water. It is a feeble base, and its salts are decomposed by water; the *hydrochloride*, $NPh(C_7H_7)_2,HCl + H_2O$, forms lustrous, prismatic crystals; the *platinochloride*, $[NPh(C_7H_7)_2]_2,H_2PtCl_6$, crystallises in thin, orange-yellow scales, and the *picrate* crystallises in long, yellow needles, melting at 131—132° with decomposition. *Nitrodibenzylaniline*, $NO_2{\cdot}C_6H_4{\cdot}N(C_7H_7)_2$ [$NO_2 : N = 1 : 4$], is formed when dibenzylaniline in acetic acid solution is nitrated in the cold with the theoretical quantity of fuming nitric acid. It crystallises in yellow needles, melts at 130°, and is soluble in ether and benzene, sparingly soluble in hot alcohol. Nitrodibenzylaniline is destitute of basic properties, and is unaltered when boiled with hydrochloric acid or aqueous soda. On reduction with tin and hydrochloric acid it yields *amidodibenzylaniline*, which crystallises in colourless, lustrous needles, melts at 89—90°, and is soluble in ether and hot alcohol. The base becomes coloured brown on exposure to air, and yields with feeble oxidising agents, such as ferric chloride, an intense red colour, which gradually changes, particularly on heating, to a dark yellow; but if sulphuric acid is present, ferric chloride forms with the base a blue precipitate insoluble in water. When heated with hydrochloric acid it decomposes into benzyl chloride and 1 : 4 diamidobenzene. Amidodibenzylaniline combines with benzaldehyde in the cold, forming a molecular compound, $NH_2{\cdot}C_6H_4{\cdot}N(C_7H_7)_2,CHPhO$; this is a yellow microcrystalline substance melting at 130°, and is decomposed by dilute acids into its constituents. *Nitrosodibenzylaniline*, $NO{\cdot}C_6H_4{\cdot}N(C_7H_7)_2$ [$NO : N = 1 : 4$], is obtained when a well-cooled mixture of dibenzylaniline, hydrochloric acid and alcohol is treated with amyl nitrite. It crystallises in thin plates which appear steel-blue by reflected and green by

transmitted light, melts at 91—92°, is soluble in alcohol, ether, and carbon bisulphide, and on reduction with tin and hydrochloric acid yields the above amidodibenzylaniline. W. P. W.

Benzyl-derivatives of Hydroxylamine. By F. Walder (*Ber.*, **20**, 1751—1755; compare Abstr., 1886, 796; this vol., p. 246).—The base, $N_2(C_7H_7)_4O$, previously described, when heated with hydrochloric acid for some hours at 220°, yields much benzaldehyde together with resinous substances and a little benzylamine.

Dibenzylethylamine, $NEt(C_7H_7)_2$, is obtained by the action of ethyl iodide and sodium ethoxide on dibenzylhydroxylamine. It is a pale-yellow liquid, boils about 300°, is readily soluble in alcohol, ether, and acids, and shows strongly marked basic characters. The platinochloride forms thin plates. In this reaction a crystalline base, $C_{13}H_{21}N$, of unknown constitution is also formed. It forms slender, interlaced needles, melts at 83—84°, and explodes when quickly heated. From these results it follows that the reaction with ethyl iodide is quite different to that with methyl iodide.

By the action of propyl iodide and sodium propoxide on dibenzylhydroxylamine, propyl ether, benzylamine and benzyl benzoate are formed. With ethyl iodide and sodium ethoxide it yields ethyl cetyl ether, benzyl ether, and benzylamine.

Dibenzylhydroxylamine mercurochloride, $N(C_7H_7)_2{\cdot}OH,HHgCl_3$, forms white, crystalline plates; the *picrate* crystallises in lustrous, yellow plates, and melts at 151° (corr.).

Dibenzylhydroxylamine gives, after a time, a sulphur-yellow coloration with a colourless solution of ferric chloride (compare Landwehr, this vol., p. 124). A. J. G.

Intermediate Products in the Formation of Indole from Dichlorether and Aromatic Amines. By J. Berlinerblau and H. Polikiev (*Monatsh. Chem.*, **8**, 187—191).—*Monochlorethylideneanilide*, $CH_2Cl{\cdot}CH:NPh$, is prepared by dissolving dichlorether in an equal volume of water, adding water, and boiling for 15 to 30 minutes. As soon as it is cold an aqueous solution of aniline is added. After some hours, the product is washed with a little water containing hydrochloric acid, and then with water alone until free from chlorine. It is an amorphous substance, insoluble in water, readily soluble in alcohol, less in ether; it melts at 86—87°. When dried until of constant weight it forms a reddish-brown powder melting at 135—136°. When treated with potassium nitrite and dilute hydrochloric acid in the cold, a yellowish-brown, amorphous compound is obtained which gives a green and then a greenish-blue solution when treated with phenol and sulphuric acid. The colour changes to red when the solution is diluted with water, but returns to green on addition of alkali.

Anilidoethylideneanilide, $NPh:CH{\cdot}CH_2{\cdot}NHPh$, is obtained by heating monochlorethylideneanilide (4 grams) with aniline (5 grams) in a small flask on a sand-bath. It dissolves rather readily in alcohol and ether, and melts at 103—105°.

Monochlorethylideneparatoluide, $CH_2Cl{\cdot}CH:N{\cdot}C_6H_4Me$, is prepared

by dissolving 22 grams of dichlorether in 20 c.c. of water, adding 180 c.c. of water, and boiling for 20 to 30 minutes. 33 grams of paratoluidine dissolved in a little alcohol and suspended in 1 litre of water is added. As soon as the whole becomes turbid it is filtered as quickly as possible and left for four to five hours. It resembles monochlorethyleneanilide, and melts at 58°. N. H. M.

Action of Chloracetic Chloride on Orthamidophenol. By O. Aschan (*Ber.*, **20**, 1523—1524). — *Chloracetamidophenol*, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Cl$, is obtained by the action of chloracetic chloride on orthamidophenol dissolved in benzene. It crystallises in large plates of a silvery lustre, and melts at 136°. It dissolves readily in aqueous alkali; when the solution is boiled a *compound* melting at 169° is obtained probably of the formula $C_6H_4<^{NH\cdot CO}_{O-CH_2}>$. When chloracetamidophenol is heated at 170° it is converted with effervescence into an oil. This contains chlorine, and has a powerful odour.

By fusing anhydrous oxalic acid with orthamidophenol at 140—150° a compound melting at 272° is formed. N. H. M.

Action of Cinnamic Acid on Diphenylamine in Presence of Zinc Chloride. By A. Bernthsen (*Ber.*, **20**, 1552—1554).— When a mixture of cinnamic acid (100 grams), diphenylamine (100 grams), and zinc chloride (250 grams), is heated for 1½ to 2 days at 240—250°, phenylacridine and a compound melting at 127—128° are obtained.

Cinnamyldiphenylamine, $CHPh:CH\cdot CO\cdot NPh_2$, is prepared by heating diphenylamine (2 mols.) with crude cinnamyl chloride. It crystallises from alcohol in yellowish needles melting at 152—153°.

N. H. M.

Action of Œnanthaldehyde and Heptyl Chloride on Dimethylaniline in the Presence of Zinc Chloride. By V. Auger (*Bull. Soc. Chim.*, **47**, 42—51).—A base of the constitution $C_6H_{13}\cdot CH(C_6H_4\cdot NMe_2)_2$ is formed by treating dimethylaniline and zinc chloride with œnanthaldehyde. It crystallises from alcohol in long needles, is but slightly soluble in cold alcohol, insoluble in water, melts at 59·5°, and boils at 275° under 15 mm. pressure. The platinochloride is but sparingly soluble in water and insoluble in alcohol and ether. Attempts to obtain a carbinol from the base by oxidation were unsuccessful, as it was invariably decomposed, œnanthaldehyde and œnanthylic acid being formed.

On treating a mixture of equal parts of dimethylaniline and zinc chloride with chloroheptane, two compounds are formed: the first is a leuco-base having the composition $C_{23}H_{32}N_2$, it melts at 72·5° and boils without decomposition at 278° under 15 mm. pressure; the platinochloride cannot be prepared in aqueous solutions, as platinum chloride acts as an oxidising agent, and a blue precipitate of the platinochloride of the oxidised base is formed; prepared from an alcoholic solution, however, it forms pale-yellow, sparingly soluble crystals. On heating the base with methyl iodide in a sealed tube at 100°, the salt $C_{23}H_{32}N_2,2MeI$ is obtained; it forms long, silky needles,

has a very bitter taste, and is decomposed by heat into the base and methyl iodide. On oxidising the leuco-base with ferric chloride, a blue hydrochloride of the base $C_{23}H_{30}N_2$, is formed; it crystallises in microscopic tables which have a bronze lustre, and is readily soluble in water, forming an indigo-blue coloured solution, but cannot be crystallised from this solvent as it spontaneously decomposes after a short time; the *iodide*, $C_{23}H_{30}N_2,HI$, however, which may be precipitated by the addition of potassium iodide to the aqueous solution of the chloride, is more stable, and may be crystallised from hot dilute alcohol, forming small prisms having a green lustre.

On reducing the base, $C_{23}H_{30}N_2$, with zinc in an acid solution, the leuco-base is again formed. The dehydrated base seems to form colourless acid salts, as on adding excess of acid to the blue solutions of the normal salts, the colour disappears but returns again on dilution or neutralisation. The blue solutions dye cotton and silk a brilliant blue, which is not, however, permanent. On adding even dilute solutions of potash or soda to the blue solutions, they become colourless, a red powder is precipitated, and a strong odour of ammoniacal bases is perceptible.

The second compound formed by the action of chloroheptane on dimethylaniline in the presence of zinc chloride is *dimethamidophenyl hexyl ketone*, $C_6H_{13}\cdot CO\cdot C_6H_4NMe_2$; when crystallised from alcohol it forms long, colourless needles; it melts at 48·5°, and boils at 190° under 20 mm. pressure. The corresponding acetoxime, $C_{15}H_{23}\cdot NOH$, was prepared; it crystallises in brilliant, colourless plates, and melts at 99°. By acting on the ketone with cold concentrated acid, the mononitro-derivative, $C_6H_{13}\cdot CO\cdot C_6H_3(NO_2)\cdot NMe_2$, is obtained; it crystallises in yellow, silky needles and melts at 65°.

As both of the above compounds have such high molecular weights, the author confirmed their formula by preparing that first described synthetically from diphenylheptane by the following process. The diphenylheptane was nitrated and dinitrophenylheptane,

$$C_6H_{13}\cdot CH : (C_6H_4NO_2)_2,$$

obtained in the form of a heavy pale-yellow oil, and by reducing this with tin and hydrochloric acid, diamidodiphenylheptane,

$$C_6H_{13}\cdot CH : (C_6H_4NH_2)_2,$$

was obtained; this base is a heavy oil which becomes coloured when exposed to the air; its nitrate crystallises in small and brilliant tablets. By heating the free base with excess of methyl alcohol and methyl iodide in a sealed tube at 100° for three hours, the tetramethyl compound is obtained and agrees in every respect with the compound obtained by the action of œnanthaldehyde on dimethylaniline in the presence of zinc chloride.

In the course of this research the following compounds were also prepared:—

Nitroheptylbenzene, $C_7H_{15}\cdot C_6H_4\cdot NO_2$, prepared by the nitration of heptylbenzene at the ordinary temperature; it is a heavy straw-coloured oil, boiling at 178° under 10 mm. pressure.

Amidoheptylbenzene, $C_7H_{15}\cdot C_6H_4\cdot NH_2$, obtained by the reduction of the last compound, is a heavy oil boiling at 175° under 10 mm. pressure; its stannochloride crystallises in needles.

Hexyl phenyl ketone, $C_6H_{13}\cdot CO\cdot Ph$, obtained by the action of aluminium chloride on a mixture of chloroheptane and benzene, crystallises in large, colourless plates, has a faint aromatic odour, melts at 17°, and boils at about 267° under 740 mm. pressure; the corresponding acetoxime crystallises in slender needles and melts at 55°.

A. P.

Tetramethyldiamidothiobenzophenone. By O. Baither (*Ber.*, **20**, 1731—1739).—This substance, $CS(C_6H_4\cdot NMe_2)_2$, or possibly, $NMe_2\langle{}^{C_6H_4}_{S}\rangle C\cdot C_6H_4\cdot NMe_2$, as its intense colour scarcely agrees with its being a simple ketone, is prepared commercially but has not yet been described. It crystallises in fine ruby-red plates with blue lustre and melts at 202°. It is soluble in benzene, carbon bisulphide (1·15 in 100), acetic acid, chloroform (4·58 in 100), less in ether (0·27 in 100), and still less in alcohol (0·072 in 100), insoluble in water and light petroleum. It can be volatilised in small quantity, but the vapour-density could not be determined. Salts could not be prepared, as hydrochloric acid converts it into tetramethyldiamidobenzophenone, and platinum chloride gives a precipitate which does not contain sulphur. With hydroxylamine it yields the oxime of tetramethyldiamidobenzophenone described by Münchmeyer (Abstr., 1886, 877). The *methiodide*, probably $NMe_2\langle{}^{C_6H_4}_{S}\rangle C\cdot C_6H_4\cdot NMe_3I$, forms cantharidine-green plates of coppery lustre, decomposes at 108°, dissolves in water with deep bluish-green colour and red fluorescence, in alcohol with green colour, and is very little soluble in ether. It dyes silk green. Aqueous soda only decomposes it to a slight extent at summer temperature, giving the free base, a yellowish-white substance, soluble in ether.

No definite bromo-derivatives were obtained from the thioketone. When distilled with zinc-dust it yields dimethylaniline and tetramethyldiamidodiphenylmethane.

When treated in carbon-bisulphide solution with thiocarbonyl chloride, $CSCl_2$, it is converted into a very unstable colouring matter, probably $NMe_2Cl\langle{}^{C_6H_4}_{S}\rangle C(CSCl)\cdot C_6H_4\cdot NMe_2$. This forms a black powder, which dissolves in water to a deep blue solution, but the colour soon disappears. If the reaction is conducted in chloroform solution and the liquid allowed to remain for some time, the colour gradually disappears, and thick, white, crystalline crusts of a decomposition product, $CCl_2(C_6H_4\cdot NMe_2)_2 + CHCl_3$, separate, which is decomposed by water.

A. J. G.

Action of Monatomic Aldehydes of the Fatty Series on Metaparatoluylenediamine. By O. Hinsberg (*Ber.*, **20**, 1585—1591).—Crystallographic examination of benzylbenzenyldiamidotoluene

(monobenzylanhydrobenzoyldiamidotoluene, Abstr., 1886, 943) establishes its identity with Ladenburg's tolubenzaldehydine (Abstr., 1878, 571).

Ethylethenyldiamidotoluene is obtained, together with small quantities of ethenyldiamidotoluene, when metaparatoluylenediamine (1 mol.), dissolved in acetic acid, is treated in the cold with acetaldehyde (2 mols.); the solution is allowed to remain for an hour, heated to remove any excess of aldehyde, precipitated with ammonia, and the base extracted with ether. After evaporation of the ether, the base is saturated with strong hydriodic acid, and from the resulting solution the hydriodide separates after some time. The base is identical with that obtained by Hübner (Abstr., 1882, 505) by ethylating ethenyldiamidotoluene.

Isobutenyldiamidotoluene, $C_7H_6<\overset{\text{---N}}{\text{NH}}>C\cdot CHMe_2$, is the chief product obtained when a cold solution of metaparatoluylenediamine in dilute acetic acid is treated with an aqueous or alcoholic solution of isobutyl alcohol until the whole of the diamine has entered into combination; after filtration from the insoluble compound formed at the same time, the solution is precipitated with ammonia and the base purified by the repeated recrystallisation of its tartrate. It crystallises in colourless needles, melts at 157—158°, is readily soluble in alcohol and ether, sparingly soluble in water, and has an intensely bitter taste. Its salts generally are very soluble in water with the exception of the platinochloride and the ferrocyanide; the *tartrate*, $C_{11}H_{14}N_2,C_4H_6O_6 + 2H_2O$, crystallises in white needles, melts at 98°, and is also sparingly soluble in water.

The insoluble compound obtained in the foregoing reaction consists of *isobutylisobutenyldiamidotoluene*, $C_7H_6<\overset{\text{---------N}}{\text{N}(C_4H_7)}>CPr$; it is formed in relatively small quantity, and has not been obtained pure. Its *hydrochloride*, $C_{15}H_{22}N_2,HCl$, forms large, colourless crystals.

Propaldehyde and œnanthaldehyde also yield very stable compounds with orthodiamines. The formation of these anhydro-compounds is not materially influenced by the presence or absence of solvents, and it is immaterial whether the aldehyde is added to the diamine or *vice versâ*. W. P. W.

Diazo-compounds. By P. Griess (*Ber.*, **20**, 1528—1531).—*Paratriazobenzenesulphonic acid phenylhydrazine*,

$$\overset{\text{N}}{\text{N}}>N\cdot C_6H_4\cdot SO_3H,NHPh\cdot NH_2 + H_2O,$$

is readily obtained by mixing an aqueous solution of phenylhydrazine with paradiazobenzenesulphonic acid, and leaving the whole for some hours. The mother-liquor is poured off, the crystals pressed between filter-paper and crystallised from hot water. It forms long, narrow, yellowish-white, lustrous plates, rather readily soluble in hot water and in hot alcohol, insoluble in ether and chloroform. When heated it detonates. Alkalis decompose it into phenylhydrazine and paratriazobenzenesulphonic acid.

Paratriazobenzenesulphonic acid, $\ll^{N}_{N}>N\cdot C_6H_4\cdot SO_3H$, is prepared from the barium salt, and forms white, deliquescent needles, very soluble in alcohol. The *barium salt*, with 2 mols. H_2O, is obtained from the phenylhydrazine-compound by boiling with barium carbonate. It crystallises in almost white, hexagonal plates.

Triazonaphthalenesulphonic acid, $N_3\cdot C_{10}H_6\cdot SO_3H$, is obtained from its phenylhydrazine-compound in a manner similar to triazobenzenesulphonic acid, and crystallises in white needles, very soluble in alcohol and in water. The *barium salt* forms white plates of a silvery lustre, very sparingly soluble. The *phenylhydrazine compound* resembles the corresponding triazobenzene-derivative in its chemical and physical behaviour. N. H. M.

Constitution of Diazoamido-compounds. By R. Meldola (*Phil. Mag.* [5], **32**, 513—529).—Only one diazoamido-compound of the constitution $X\cdot N_2\cdot NHY$ is known, whichever radicle has been first diazotised, whilst three ethyl-derivatives are known: (1) prepared by diazotising $X\cdot NH_2$ and combining with $Y\cdot NHEt$; (2) by diazotising $Y\cdot NH_2$ and combining with $X\cdot NHEt$; and (3) by directly replacing the H in the compound $X\cdot N_3H\cdot Y$ by ethyl. These facts cannot be reconciled with the usual formula of Kekulé. The conditions to be fulfilled by any formula are: (1) that it should be symmetrical so as to represent the identity of the mixed diazoamido-compounds; (2) that it should be capable of representing more than two isomeric alkyl-derivatives of mixed compounds. Griess' formula, $C_6H_4 : NH : NH : NH : C_6H_4$, is objected to, since it represents diazoamido-benzene as a phenylene-derivative, and contains three replaceable hydrogens, whilst the dinitrodiazoamido-compounds point to only one being present, and it does not represent the easy resolution of diazoamido-compounds by acids. Victor Meyer's abandoned formula, $NH<^{NX}_{NY}>$, fails to represent the N of the NH as being directly attached to either of the radicles. The formulæ $\ll^{N}_{N}>NHXY$ and $N : N : NHXY$, due to the author, are also discarded, as they do not represent the decomposition by acids or the existence of isomeric alkyl-derivatives. Finally the formula $NH\ll^{X\cdot N}_{Y\cdot N}\gg$, in which the phenyl of the radicles X and Y is regarded as triatomic, is considered best to represent the reactions of the mixed diazoamido-compounds, the phenyl having the constitution $=C<^{CH : CH}_{CH : CH}>CH$—in accordance with Fittig's theory of the constitution of quinone. The third ethyl-derivative of the mixed diazoamido-compounds can now be considered to be formed by the replacement of the nitrogen-attached hydrogen of the above formula, whilst, owing to the symmetry of the formula, the same mixed diazoamido-compound will be formed irrespective of the order of combination. Again, by supposing the $N : N$ to be eliminated with the radicles X and Y in turn, the production of two diazo- and two diamido-compounds by means of hydrochloric acid is explained. On

the other hand, this formula does not satisfactorily represent the normal compounds. In representing the compound obtained from diazotised paranitraniline or para-ethylnitraniline as

$$NH<\begin{matrix}C_6H_4(NO_2)\cdot N\\ C_6H_4(NO_2).N\end{matrix}>,$$

the ethyl-derivatives from diazotised paranitraniline and meta-ethylaniline and from diazotised metanitraniline and para-ethylaniline should have a similar constitution, but the formula being symmetrical the compounds would be identical, whereas they are undoubtedly isomeric. Although Kekulé's formula accurately represents the reactions of the normal compounds, their stability is at variance with such a chain formula, no other instance of which is known amongst nitrogen compounds, the author therefore prefers the formula $N<\begin{matrix}N\\ X\end{matrix}>NHX$, the compound splitting when decomposed, so as to leave the N : N in combination with the lower X, and thus giving only two products. The para-position is chosen for the free bonds in the radicle C_6H_5''', in accordance with the conversion of diazoamidobenzene into amidazobenzene, in which the substituents hold the para-position. H. K. T.

Diazoamido-compounds. By B. Fischer and H. Wimmer (*Ber.*, **20**, 1581—1583).—A comparison of the methods proposed by Fischer (Abstr., 1884, 1014), and by Staedel and Bauer (Abstr., 1886, 943), for the preparation of diazoamidobenzene shows that they are equally satisfactory in this particular, but that the former is to be preferred when mixed diazoamido-compounds are required. The melting point of the diazoamidobenzene prepared by either method is 98°, and the product obtained by Fischer's method is free from amidoazobenzene. Diazoamidoparatoluene can also be readily prepared from paratoluidine under the same conditions.

Diazoamido-orthotoluene is formed when orthotoluidine (2 mols.) is dissolved in hydrochloric acid (3 mols.) and water (3 mols.), the solution cooled to −5°, and treated with a solution of sodium nitrite (1 mol.), sodium acetate being added as required to remove the hydrochloric acid set free. The temperature is maintained at −5° for six hours; the crystals of diazoamido-orthotoluene are then separated, drained on a tile, dissolved in cooled alcohol, and thrown out of solution in the crystalline form by addition of ice. It is an orange-yellow, crystalline powder, melts at about 50°, and decomposes even during the spontaneous evaporation of its solutions in various media, such as alcohol, ether, &c.

Diazoamidoxylene, prepared from xylidine by a similar method, separated as an oil, and could not be obtained in a crystalline state. W. P. W.

Hydroxyazo-compounds. By B. Fischer and H. Wimmer (*Ber.*, **20**, 1577—1581).—The authors, working on similar lines to Heumann and Œconomides (this vol., pp. 480, 684), have independently obtained hydroxyazo-compounds by the addition of a diazoamido-derivative (1 mol.) to a phenol (1 mol.) in the fused state. In this way orthotolueneazoresorcinol is formed from diazoamido-orthotoluene and

resorcinol, and a *xyleneazoresorcinol*, $C_8H_9{\cdot}N_2{\cdot}C_6H_3(OH)_2$, from diazoamidoxylene and resorcinol; the latter compound crystallises from alcohol in fiery-red needles, and melts at 205—206°; it is identical with the azo-compound prepared by the action of diazoxylene chloride on resorcinol.

Under similar conditions diazoamidobenzene, diazoamido-orthotoluene, and diazoamidoparatoluene when added to fused β-naphthol yield benzeneazo-β-naphthol, orthotolueneazo-β-naphthol, and paratolueneazo-β-naphthol respectively (this vol., p. 55). W. P. W.

Unsymmetrical Benzoylphenylhydrazine. By A. Michaelis and F. Schmidt (*Ber.*, **20**, 1713—1718).—The doubt expressed in the author's first communication (this vol., p. 365) as to the constitution of this compound has now been removed, as it has been found that it unites readily with benzaldehyde and with acetone, with elimination of water; it must therefore contain a nitrogen-atom in union with two hydrogen-atoms, that is, have the formula $NPhBz{\cdot}NH_2$. The author suggests that phenylhydrazine-derivatives, where substitution occurs in the NH-group, shall be termed α-compounds, the term β-compounds being applied to the symmetrical derivatives in which substitution has occurred in the NH_2-group. The statement (*loc. cit.*) as to the difference in behaviour of the authors' dibenzoylphenylhydrazine with that described by Fischer was due to a misprint in Fischer's paper; the substances are identical.

The following salts of α-benzoylphenylhydrazine are described: the *hydrobromide* melts at 191°; the *sulphate* crystallises in groups of slender needles and melts at 191°. The *nitrate* forms long, lustrous plates and melts at 145°; the *picrate* melts at 122°.

When treated with nitrous acid in strongly acid solution, α-benzoylphenylhydrazine is converted into benzoylaniline and nitrous oxide, in neutral solution, on the other hand, it yields diazobenzenimide and benzoic acid.

α-Benzoyl-β-acetylphenylhydrazine, $NPhBz{\cdot}NHAc$, obtained by the action of acetic anhydride on the base, crystallises in long needles and melts at 152—153°; it is also obtained by the action of benzoic chloride on β-acetylphenylhydrazine.

Benzoylphenylsemicarbazide, $NPhBz{\cdot}NH{\cdot}CO{\cdot}NH_2$, is obtained by the action of potassium cyanide on a feebly acid solution of a salt of the base. It forms crystalline crusts, melts at 202—203°, and is sparingly soluble in benzene, readily in alcohol. *Diphenylbenzoylthiosemicarbazide*, $NPhBz{\cdot}NH{\cdot}CS{\cdot}NHPh$, is prepared by the action of phenylthiocarbimide on the base. It is crystalline, melts at 310°, and is sparingly soluble in ether, benzene, chloroform, and hot alcohol.

Benzylidenebenzoylphenylhydrazide, $NPhBz{\cdot}N : CHPh$, is prepared by gently heating a mixture of benzaldehyde and benzoylphenylhydrazine; it crystallises in very thin needles of silky lustre, melts at 122°, is nearly insoluble in water, readily in alcohol, and only reduces Fehling's solution after long boiling.

Acetonebenzoylphenylhydrazide, $NPhBz{\cdot}N : CMe_2$, separates after a time from a hot solution of benzoylphenylhydrazine in acetone, after dilution with water. It forms lustrous prisms, melts at 115·5°, and

is very soluble in acetone and alcohol, more sparingly in ether, scarcely soluble in water. *Acetophenone benzoylphenylhydrazide*, NPhBz·N : CMePh, is obtained after a long time from a mixed alcoholic solution of its constituents; it crystallises in colourless needles, melts at 124°, and is readily soluble in alcohol, insoluble in water.

Acetylbenzylidenephenylhydrazine, NPhAc·N : CHPh, is mentioned but not described. A. J. G.

Manufacture of Methyl-violet. By O. Mühlhäuser (*Dingl. polyt. J.*, **264**, 37—45).—For the production of this dye 20 kilos. of methylaniline and 8 kilos. of phenol are heated at 55° with 175 kilos. of rock salt and 10 kilos. of copper sulphate. The operation is conducted in cast-iron cylinders provided with agitators. The oxidation-product is then washed with water and treated with milk of lime when the salt and phenol are dissolved, whilst the methyl-violet, copper hydroxide, and calcium sulphate are precipitated. The mixture is filtered and washed, and the precipitate saturated with hydrogen sulphide. The copper is thereby converted into the sulphide, and the dye separated from it by means of hydrochloric acid. The violet solution is then treated with a filtered solution of salt, which precipitates the colouring matter as a green tarry mass. This is purified by solution in hot water and reprecipitation with salt solution. The purified product is washed with water, dried and ground. It is then made up into the different brands (violet 3 B, 4 B, and 5 B) by the addition of benzyl-violet. The methyl-violet obtained by this method consists of a mixture of tetra- and penta-methylpararosaniline. D. B.

Induline and Azophenine. By O. N. Witt (*Ber.*, **20**, 1538—1541).—Azophenine (Thomas and Witt, Trans., 1883, 117) is best prepared by heating amidoazobenzene (2 parts), aniline hydrochloride (1 part), and aniline (4 parts) for 24 hours at 80—90°; it is washed with alcohol and crystallised from alcohol. When the heating is continued for 12 to 20 hours at 125—130°, the product consists of induline, $C_{18}H_{15}N_3$, together with the higher induline, $C_{30}H_{23}N_5$ and its phenyl-derivative, $C_{36}H_{27}N_5$. Azophenine is also formed by the action of free nitrosodimethylaniline and nitrosodiethylaniline on aniline. If the aniline is replaced by toluidine, azoparatoline (Nölting and Witt, Abstr., 1884, 742) is obtained.

When azophenine is heated at 360°, it is decomposed into aniline, fluorindine, and a violet dye. When reduced with tin and hydrochloric acid, it yields aniline and a sparingly soluble hydrochloride of an unstable base. It is concluded that azophenine is an azo-dye, formed by the dehydrogenation of aniline, and that it contains on the one side of one or several azo-groups, the radicle phenyl, on the other side, an unknown radicle.

When induline is distilled with lime, the greater part is carbonised and a distillate is obtained containing carbazole, together with aniline, benzene, and diphenylamine; induline is therefore a diphenylamine-derivative. N. H. M.

Roshydrazine and a New Class of Dyes. By J. H. Ziegler (*Ber.*, **20**, 1557—1558).—When 5 grams of rosaniline dissolved in 30 c.c. of strong hydrochloric acid and 70 c.c. of water is treated with 3·5 grams of sodium nitrite, and the whole then added to a solution of 12 grams of tin in 30 c.c. of hydrochloric acid, the hydrazine salt separates in green crystals, readily soluble in water, almost insoluble in strong hydrochloric acid. The yield is 13 grams. The shade of the salt of the new hydrazine, which is called *roshydrazine*, is somewhat more blue than that of magenta. The solution reduces Fehling's solution in the cold. It readily forms condensation-products with ketones and aldehydes. Formic acid yields a red compound, acetone, aldehyde, pyruvic acid, and benzophene, red to blue-violet compounds, benzaldehyde and ethyl acetoacetate, blue dyes. The dyes dissolve readily in alcohol, sparingly or not at all in water.

N. H. M.

Aniline Sebate and Diphenyl-sebacamide. By G. Gehring (*Compt. rend.*, **104**, 1451—1452).—When aniline (2 mols.) is mixed with sebacic acid (1 mol.), dissolved in alcohol, complete combination takes place without separation of water, and with formation of aniline sebate, $(C_6H_7N)_2C_{10}H_{18}O_4$, which is obtained by evaporation in a vacuum, and is purified by recrystallisation from hot water. It then forms thin, colourless, highly lustrous, rhomboidal lamellæ, which are only slightly soluble in cold, but more soluble in hot water, very soluble in cold alcohol, and somewhat soluble in boiling ether or chloroform. Aniline sebate melts at 134°, and sublimes without decomposition. It dissolves in concentrated sulphuric acid, and the solution gives the colour reactions for aniline with oxidising agents.

Aniline sebate does not lose water and form an anilide even at 250°. If, however, equal parts of aniline and sebacic acid are heated together, the temperature being gradually raised to 215°, diphenylsebacamide, $(PhNH)_2C_{10}H_{16}O_2$, is obtained, and is purified by recrystallisation from alcohol. It forms colourless, odourless, tasteless, rhombic scales, which melt at 198° and distil without decomposition above 360°. It is insoluble in water and light petroleum, and only very slightly soluble in boiling ether, but dissolves in alcohol, chloroform, and benzene. Phenyl sebacamide is not attacked by alcoholic potash, but when fused with potash it yields aniline. It dissolves in concentrated nitric and sulphuric acids, but is precipitated unchanged on addition of water. When heated with concentrated nitric acid in sealed tubes, it yields a nitro-derivative which crystallises in needles.

C. H. B.

Action of Thiocarbonyl Chloride on Secondary Amines. By O. Billeter (*Ber.*, **20**, 1629—1632).—*Ethylphenylthiocarbamine chloride*, CSCl·NPhEt, is obtained when ethylaniline (1 mol.) is shaken with thiocarbonyl chloride (1 mol.) dissolved in chloroform. It crystallises in long prisms, melts at 56·5—57°, and is extremely soluble in chloroform, readily soluble in light petroleum and ether. Alcohol at first dissolves the compound without change, but decomposes it slowly in the cold or quickly on heating into ethylaniline hydrochloride, an oil containing sulphur, ethyl chloride, and *ethylphenylthiocarbamine oxide*, $(CS{\cdot}NPhEt)_2O$. This crystallises in com-

pact, citron-yellow needles or prisms, melts at 143—143·5°, and is soluble in ether and light petroleum, readily soluble in boiling alcohol; 100 parts of alcohol dissolve 0·7 part of the oxide at 15°.

Methylphenylthiocarbamine chloride, CSCl·NPhMe, prepared similarly to the ethyl-compound, forms pale-yellow crystals, melts at 34·5—35°, and is soluble in light petroleum; if heated with alcohol it yields *methylphenylthiocarbamine oxide*, $(CS{\cdot}NPhMe)_2O$, in sulphur-yellow crystals, melting at 116·5°.

When either ethyl- or methyl-phenylthiocarbamine chloride (1 mol.) is heated with ethyl- or methyl-aniline (2 mols.) at 100°, a considerable rise of temperature occurs and tetra-substituted thiocarbamides are obtained; these are soluble in light petroleum and alcohol, but insoluble in alkalis. *Diethyldiphenylthiocarbamide*, $CS(NPhEt)_2$, crystallises from light petroleum in white tables, from alcohol in long needles or prisms, and melts at 75·5°; the *dimethyl*-derivative forms monoclinic crystals and melts at 72·5°, and the *methylethyl*-derivative crystallises in forms resembling those of the methyl-derivative, and melts at 49·5°. W. P. W.

Orthamidophenyl Mercaptan. By A. W. Hofmann (*Ber.*, **20**, 1788—1797).—The action of carbon bisulphide on orthamidophenyl mercaptan or the corresponding disulphide gives, not as was expected, a thiocarbamide, but a mercaptan of the formula $C_6H_4{<}\overset{N}{\underset{S}{>}}C{\cdot}SH$. This crystallises in lustrous, colourless needles, melts at 179°, has an intensely bitter taste, and is insoluble in water, soluble in alcohol, ether, and acetic acid. Proof of its constitution is given by its formation by the action of chlorophenylthiocarbimide on sodium hydrosulphide, and by its decomposition into orthamidophenyl mercaptan, carbonic anhydride, and hydrogen sulphide when fused with potash. The corresponding *disulphide*, $S_2(C_7H_5NS)_2$, is obtained by adding potassium dichromate to an acetic acid solution of the compound. It forms silvery plates, melts at 180°, and is converted into a black, amorphous substance when further oxidised. The *methyl ether*, $C_7H_5NS{\cdot}SMe$, crystallises in short, colourless prisms and melts at 52°; it forms unstable salts, the platinochloride,

$$(C_7H_5NS{\cdot}SMe)_2,H_2PtCl_6,$$

crystallises in lustrous plates.

Thioanisidine, $NH_2{\cdot}C_6H_4{\cdot}SMe$, is prepared by the action of methyl iodide on orthamidophenyl mercaptan, and subsequent hydrolysis of the resulting hydriodide. It is a colourless liquid, distils with some decomposition at 234°, and yields well-defined salts, which can be recrystallised from water. The hydrochloride forms colourless needles.

Dithioanisylthiocarbamide, $CS(NH{\cdot}C_6H_4{\cdot}SMe)_2$, is prepared by digesting thioanisidine with carbon bisulphide for some hours in a reflux apparatus; it crystallises in small, colourless prisms, and melts at 162°; when further heated it yields *thioanisylthiocarbimide*,

$$NCS{\cdot}C_6H_4{\cdot}SMe,$$

and thioanisidine. The former is a light-yellow oil of burning taste, which boils about 270°, but could not be obtained pure. With alcoholic ammonia it yields *thioanisylthiocarbamide*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_4\cdot SMe,$$

a substance crystallising in prisms and melting at 168°.

Anisylthiocarbimide, $NCS\cdot C_6H_4\cdot OMe$, is obtained by distilling dianisyl thiocarbamide; it boils at 264—266°, and when treated with alcoholic ammonia is converted into *anisylthiocarbamide*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_4\cdot OMe,$$

which crystallises in colourless needles melting at 152°.

When a mixture of amidophenyl mercaptan and phenylthiocarbimide is heated, the substance previously described by the author (Abstr., 1880, 388) as anilidophenylthiocarbimide is obtained, he now regards it as having the constitution $C_6H_4<\overset{N}{\underset{S}{>}}C\cdot NHPh$.

When an ethereal solution of amidophenyl mercaptan is mixed with ethyl chlorocarbonate, a colourless oil is obtained, which from its mode of formation and properties would seem to have the composition $SH\cdot C_6H\cdot NH\cdot COOEt$. When distilled it yields alcohol and Hofmann's hydroxyphenylthiocarbimide. A. J. G.

Xylyl Phosphorous Compounds: Toluphosphinic Acids. By J. Weller (*Ber.*, **20**, 1718—1725. Compare Michaelis and Paneck, Abstr., 1882, 958).—*Mercury dixylyl*, $Hg(C_6H_3Me_2)_2$ [$Hg : Me_2 = 4 : 1 : 3$], is obtained by heating bromometaxylene with 2 per cent. sodium amalgam at 140—150° for 12 hours. It crystallises in slender, felted needles, melts at 169—170°, and is sparingly soluble in ether, alcohol, and cold benzene, readily soluble in hot benzene. Hydrochloric acid on boiling readily decomposes it into mercuric chloride and metaxylene.

1 . 3 . 4 *Xylylphosphochloride*, $C_6H_3Me_2\cdot PCl_2$, is obtained by the action of phosphorous chloride on 1 : 3 : 4 mercury dixylyl at 230—240°. It is a colourless, highly refractive liquid, which fumes slightly in the air and boils at 256—258°. Water decomposes it with formation of xylylphosphinous acid. Chlorine unites vigorously with it, forming the viscous, yellow tetrachloride which is decomposed by water first into the oxychloride, then into xylylphosphinic acid melting at 194°.

By the action of phosphorous chloride on metaxylene in presence of aluminium chloride, a mixture of the preceding α-compound with smaller quantities of an isomeride, β-xylylphosphochloride [$Me_2 : PCl_2 = 1 : 3 : 5$?] is obtained. This mixture forms a colourless liquid boiling constantly at 256°, and of sp. gr. 1·24 at 18°. It absorbs chlorine to form a mixture of the tetrachlorides, which is obtained as a viscid mass having crystals interspersed through it. As the α-tetrachloride is liquid, the crystals must be those of the β-compound. When treated with sulphurous anhydride the tetrachlorides are converted into the oxychlorides which distil at 280—300°, but cannot be separated by distillation. The oxychlorides are therefore decom-

posed by long boiling with water into the corresponding metaxylylphosphinic acids, which can then be separated by crystallisation.

α-Metaxylylphosphinic acid, $C_6H_3Me_2\cdot PO(OH)_2$ [1 : 3 : 4], forms long, white needles, melts at 194°, and is very readily soluble in alcohol, more sparingly in ether. 100 parts of water dissolve 1·5 parts of the acid at 20° and 6·9 parts at 100°. When heated with alkalis it is decomposed into metaxylene and phosphoric acid. Bromine acts on it in aqueous solution with formation of phosphoric acid and a mixture of brominated metaxylenes. The barium, cadmium, nickel, and silver salts are described. The metaxylylphosphinic acid (m. p. 186—187°) obtained by Michaelis and Paneck (*loc. cit.*), was probably a mixture of this acid with some of the acid of lower melting point. When treated with nitric acid it yields two isomeric *nitro-acids*, $NO_2\cdot C_6H_2Me_2\cdot PO_3H_2$, of which one, the less soluble in water, crystallises in needles and melts at 182°, whilst the other melts at 100°.

β-Metaxylylphosphinic acid, $C_6H_3Me_2\cdot PO(OH_2)$ [1 : 3 : 5 ?], crystallises in thin plates, melts at 161°, and is soluble in alcohol and ether. 100 parts of water dissolve 1·8 parts of the acid at 15° and 117·3 parts at 100°. Its behaviour with alkalis and bromine resembles that of the *α*-acid, except that in the latter case a sparingly soluble bromoxylylphosphinic acid is also invariably formed. The salts of this acid resemble those of the *α*-acid but are somewhat more soluble. Nitric acid partly oxidises it to *β*-toluphosphinic acid, partly converts it into a nitro-acid, $NO_2\cdot C_8H_8\cdot PO_3H_2$.

α-Toluphosphinic acid, $COOH\cdot C_6H_3Me\cdot PO(OH)_2$, is prepared by oxidising *α*-metaxylylphosphinic acid in dilute alkaline solution with the calculated amount of potassium permanganate. It crystallises in colourless prisms, melts at 262°, and is readily soluble in alcohol and hot water, sparingly soluble in ether. It is a strong tribasic acid, but its salts are difficult to prepare in a pure state, as there is a tendency to form mixtures of normal and acid salts. When strongly heated it is converted with partial carbonisation into metatoluic and metaphosphoric acids. The *chloride*, $COCl\cdot C_6H_3Me\cdot POCl_2$, is a thick liquid which distils at about 310°.

β-Toluphosphinic acid melts at 220°, but otherwise resembles the *α*-acid from which, however, it is distinguished by not giving a crystalline precipitate when mixed with copper sulphate solution.

A. J. G.

Condensation of Aldehydes with Phenols. By A. Michael (*Ber.*, **20**, 1572—1573).—A reply to Claisen (*Ber.*, **19**, 3316, footnote).

Oxidation of Ketones with Potassium Ferricyanide. By K. Buchka and P. H. Irish (*Ber.*, **20**, 1762—1767).—Claus' rule, that only those aromatic methyl ketones can be oxidised to *α*-ketonic acids which contain a side-group in the ortho-position to the methyl-group (Abstr., 1886, 462), although seemingly true for oxidations with potassium permanganate, is decidedly not correct if potassium ferricyanide is employed as the oxidising agent.

When paratolyl methyl ketone is oxidised with potassium ferri-

cyanide in alkaline solution in the cold, it yields paratoluic acid and *paratolylglyoxylic acid*. The latter, $C_6H_4Me{\cdot}CO{\cdot}COOH$ [= 1 : 4], is crystalline, melts at 95—97° (uncorr.), and is not volatile. The barium salt (+ 8 mols. H_2O) and the potassium salt were prepared. It gives a crystalline compound with phenylhydrazine, melting at 144°, and when heated with concentrated sulphuric acid and benzene containing thiophen yields a red dye, in this resembling phenylglyoxylic acid. The acid when further oxidised yields terephthalic acid.

Orthoxylylglyoxylic acid, $C_6H_3Me_2{\cdot}CO{\cdot}COOH$ [Me_2 : $CO{\cdot}COOH$ = 4 : 3 : 1], is prepared in like manner from methyl orthoxylene ketone; it melts at 92° (uncorr.), and yields a barium salt crystallising in slender needles.

Methyl metatolyl ketone, prepared by distilling calcium metatoluate and acetate, boils at 218—220°, and by oxidation with potassium ferricyanide is converted into an acid not volatile with steam; this is still under investigation. A. J. G.

Cyanacetophenone. By A. Haller (*Compt. rend.*, **104**, 1448—1451).—Cyanacetophenone seems to have an acid function, and dissolves readily in alkalis, but the compounds formed are very unstable. The silver-derivative, $COPh{\cdot}CHAg{\cdot}CN$, is obtained by adding silver nitrate to a dilute alcoholic solution of cyanacetophenone neutralised with soda or ammonia. It is insoluble in water and alcohol, and is decomposed when exposed to light.

When cyanacetophenone is boiled with concentrated potash it yields ammonia, potassium benzoate, and potassium acetate. A saturated solution in absolute alcohol when cooled at 0°, and treated with hydrogen chloride, deposits white needles of the composition $C_{11}H_{14}O_2NCl$, insoluble in water and ether. This compound in all probability has the constitution $COPh{\cdot}CH_2{\cdot}C(OEt) : NH,HCl$, and is the hydrochloride of ethyl benzoylacetonitrile. With ammonia it yields ammonium chloride and ethyl benzoylacetonitrile, and with potassium nitrate it yields a corresponding nitroso-derivative, which crystallises in needles melting at 117°. When the hydrochloride is heated with dilute alcohol it yields ammonium chloride and ethyl benzoylacetate.

The action of hydrochloric acid in excess on cyanacetophenone in presence of alcohol, yields ethyl benzoate and ammonium chloride.

Ethyl cyanacetate, when treated with metallic sodium, yields the derivative $CN{\cdot}CHNa{\cdot}COOEt$, and this in contact with iodo-derivatives and acid chlorides, yields compounds of the type $CN{\cdot}CHR{\cdot}COOEt$.

C. H. B.

Isonitroso-compounds. By E. Beckmann (*Ber.*, **20**, 1507—1510; compare Abstr., 1885, 618).—The intramolecular change which takes place when diphenylketoxime is treated with phosphorous pentachloride, is also produced by strong sulphuric acid at 100°. When the product of the reaction is poured into water, the precipitate treated with sodium carbonate and recrystallised from alcohol, pure benzonitrile is obtained. When the latter is heated for some time with sulphuric acid, benzoic acid and aniline are formed.

Methylphenylketoxime yields acetanilide when heated with sulphuric acid.

Benzaldoxime (2·5 parts) when poured into a mixture of 10 parts of sulphuric acid and 1 part of water, is converted into benzamide, and not into formonitrile, as was expected.

In a similar manner the dioxime of benzil is converted by sulphuric acid into a crystalline compound melting at 110°. N. H. M.

Aromatic Ethylenediketones and Alkylated Benzoyl-β-propionic Acids. By A. Claus and others (*Ber.*, **20**, 1374—1378).—The authors have obtained the above compounds by the action of succinic chloride on aromatic hydrocarbons in the presence of aluminium chloride. When 1 mol. of the hydrocarbon is used, the chief product obtained is a benzoylpropionic acid, whilst with 2 mols. of hydrocarbon it is a diketone.

I. By Claus and Werner.—*Diphenyl ethylene diketone*,

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}Ph,$$

prepared from benzene, crystallises in colourless needles, insoluble in water, soluble in alcohol, ether, and benzene, and melting at 140°. Benzoyl-β-propionic acid melts at 116°, and has already been obtained by Burker (Abstr., 1881, 273). *Dimetaxylyl ethylene diketone*, $C_2H_4(CO{\cdot}C_6H_3Me_2)_2$ [CO : Me : Me = 1 : 2 : 4], prepared from metaxylene, forms colourless needles, soluble in alcohol, ether, and chloroform, and melting at 129°. With phenylhydrazine, it yields a *dihydrazide*, crystallising in orange needles melting at 189°. The *diisonitroso-derivative*, $C_{20}H_{22}(NOH)_2$, is white, and melts at 140°. When oxidised with dilute nitric acid, the diketone yields metaxylic (orthoparadimethylbenzoic) acid, thus proving the constitution to be as above. *Orthoparadimethylbenzoyl-β-propionic acid*,

$$C_6H_3Me_2{\cdot}CO{\cdot}C_2H_4{\cdot}COOH,$$

is almost insoluble in water, soluble in organic solvents. It crystallises in colourless needles melting at 108°. Several of the salts are described.

II. By Claus and Schlarb.—*Paraditolyl ethylene diketone*,

$$C_2H_4(CO{\cdot}C_6H_4Me)_2\ [CO : Me = 1 : 4],$$

crystallises in colourless needles melting at 159°. Nitric acid oxidises it to paratoluic acid. *Paratoluyl-β-propionic acid*,

$$C_6H_4Me{\cdot}CO{\cdot}C_2H_4{\cdot}COOH,$$

crystallises from water in minute needles melting at 127°. *Dipseudocumyl ethylene diketone*, $C_2H_4(CO{\cdot}C_6H_2Me_3)_2$, forms crystals melting at 120°, and yielding, with nitric acid, 2 : 4 : 5 trimethylbenzoic acid. 2 : 4 : 5 *Trimethylbenzoyl-β-propionic* (*pseudocumyl-γ-ketonic*) *acid*, $C_6H_2Me_3{\cdot}CO{\cdot}C_2H_4{\cdot}COOH$, forms colourless crystals melting at 105°.

III. By Claus and Murtfeld.—*Diparaxylyl ethylene diketone*, $C_2H_4(CO{\cdot}C_6H_3Me_2)_2$, forms needles melting at 123°. *Paraxylyl-γ-ketonic acid*, $C_6H_3Me_2{\cdot}CO{\cdot}C_2H_4{\cdot}COOH$, forms colourless needles melt-

ing at 84°. The corresponding derivatives of cymene are thick oils, the ketone boiling at 320°.

All the above temperatures are uncorrected. L. T. T.

Chlorobenzoic Acids. By A. Claus and A. W. Bücher (*Ber.*, **20**, 1621—1627).—β-Dichlorobenzoic acid (m. p. = 156°), obtained together with the α-acid [COOH : Cl : Cl = 1 : 3 : 4], when benzoic acid is treated with chlorine (this Journ., 1877, ii, 782), has been supposed to be identical with the dichlorobenzoic acid (m. p. = 153°), [COOH : Cl : Cl = 1 : 2 : 5], prepared by Lellman and Klotz (Abstr., 1886, 452). This view, however, is untenable, since direct comparison of the two acids shows them to be isomerides. The barium salt of Lellmann's acid crystallises in lustrous needles with $3\frac{1}{2}$ mols. of H_2O, that of the β-acid in aggregates with 3 mols. of H_2O, and Lellman's acid when heated at 220° with dilute sulphuric acid (3 vols. acid to 2 vols. water), is converted into 1 : 4 dichlorobenzene and carbonic anhydride, whilst the β-acid is not attacked even by concentrated sulphuric acid at 300°. On distillation with lime, the β-acid yields a dichlorobenzene which, when nitrated, is found to be identical with nitro-orthodichlorobenzene, hence the constitution of the acid must be [COOH : Cl : Cl = 1 : 2 : 3]. The best yield of the acid is obtained when benzoic acid ($1\frac{1}{2}$ parts) is dissolved in water (60 parts) and concentrated hydrochloric acid (10 parts), and the warm solution treated with a concentrated aqueous solution of potassium chlorate (4 parts) in small portions at a time, so that the operation takes from 30 to 40 hours for its completion. Although orthochlorobenzoic acid is present among the products of the direct chlorination of benzoic acid, yet the quantity is variable and sometimes extremely small, and this fact is considered to lend support to the conjecture that the dichlorobenzoic acid obtained by Beilstein by the chlorination of orthochlorobenzoic acid is not the β-acid, but has the constitution [COOH : Cl : Cl = 1 : 2 : 5].

The α- and β-acids are scarcely attacked by nitric acid, and not at all when in acetic acid solution, but when heated with a mixture of nitric and sulphuric acids they yield the nitrochlorobenzoic acids [COOH : Cl : NO_2 = 1 : 3 : 4] (m. p. = 137°) and [COOH : Cl : NO_2 = 1 : 3 : 2] (m. p. = 136°). Both acids can also be nitrated if they are dissolved in ordinary nitric acid and treated with sulphuric acid (1 part to 3—4 parts of nitric acid). The *dichloronitrobenzoic acid* from the α-acid forms colourless needles, melts at 160°, and is soluble in water; that from the β-acid crystallises in scales, melts at 214—215°, and is sparingly soluble in boiling water. The *barium* salt of the latter, $(C_7H_2Cl_2O_2{\cdot}NO_2)_2Ba + 4H_2O$, crystallises in lens-shaped aggregates of small needles.

The α-acid, when further chlorinated by heating with manganese dioxide and hydrochloric acid for $2\frac{1}{2}$ days at 180°, yields a trichlorobenzoic acid, which is most probably identical with the acid [COOH : Cl : Cl : Cl = 1 : 3 : 4 : 5] (m. p. = 203°). This acid can readily be obtained from trichlorobenzotrichloride (formed together with the dichloro-derivative when benzotrichloride is chlorinated in the presence of iodine) by hydrolysis with aqueous soda. As the two

compounds could not be separated, a mixture of α-dichlorobenzoic acid and trichlorobenzoic acid (m. p. = 203°) was obtained, and the acids separated by fractional crystallisation of their barium salts. The trichlorobenzoic acid formed from the β-acid by heating with manganese dioxide and hydrochloric acid has not yet been obtained pure, and is difficult to prepare, inasmuch as the action tends to result in the production of higher chlorinated acids. Both the α- and β-acid yield the same tetrachlorobenzoic acid [1 : 2 : 3 : 4 : 5], melting at 165°, which is separated from the accompanying pentachlorobenzoic acid, melting at 199—200°, by fractional crystallisation from water, in which it is the less soluble. The *barium* salts of these acids, $(C_7HCl_4O_2)_2Ba + 3\frac{1}{2}H_2O$ and $(C_7Cl_5O_2)Ba + 4H_2O$, crystallise in beautiful, stellate groups of needles. W. P. W.

Phenylacetic Acid and Desoxybenzoins. By R. Anschütz and W. Berns (*Ber.*, **20**, 1389—1393).—Contrary to the experience of Hotter and others, the authors found no difficulty in obtaining phenylacetic chloride free from phosphoric compounds. The pure chloride boils at 102·5° under 17 mm. pressure. With oxalic acid it readily yields the anhydride if the chloride is kept in excess. The anhydride melts at 72·5°, and is easily converted into the acid by moisture.

By the action of alcoholic potash on desoxybenzoin the authors obtained a compound probably identical with that obtained by Limpricht and Schwanert, and named by them diethylcarbobenzonic acid, $C_{18}H_{18}O_2$. The authors, however, ascribe the formula $C_{16}H_{16}C_2$ to this compound, which boils at 238—240° under 11 mm. pressure. They are investigating this substance further. L. T. T.

Glaser's Monobromocinnamic Acids. By R. Anschütz and C. C. Selden (*Ber.*, **20**, 1382—1388).—The authors have prepared and compared several of the derivatives of the α- and β-acids. The ethereal salts of the β-acid were prepared from the silver salt since hydrochloric or sulphuric acid converts the β- into α-acid. The *α-methyl salt* boils at 158·5—159·5° under 14 mm. pressure, at 286·5—288·5° under ordinary pressure; the *β-methyl salt* at 145—147° under 11 mm.; the *α-ethyl salt* at 186·5—188·5° under 29·5 mm.; the *β-ethyl salt* at 151—153° under 10·5 mm. Both β-salts are converted into the α-compounds by distillation under ordinary pressure. *α-Bromocinnamic chloride* is formed by the action of phosphoric chloride on either the α- or β-acid, or any of their salts. It is a clear, slightly yellow liquid, which boils at 152·4° under 12 mm. pressure. All attempts to prepare a second (β) chloride were unavailing. With ammonia the chloride yields *α-bromocinnamide*, which crystallises from water in scales melting at 118·5—119°. The *anilide* forms needles or hexagonal plates melting at 80°.

The authors consider the relations of the two acids to one another to be the same as those between maleic and fumaric acids.

L. T. T.

Metamethylcinnamic Acid. By E. Bornemann (*Ber.*, **20**, 1382).—Referring to Müller's paper (this vol., p. 734) the author

points out that he obtained the above acid three years ago (Abstr., 1884, 1163).

Isomerism in the Cinnamic Acid Series. By W. Roser and E. Haseloff (*Ber.*, **20**, 1576—1577).—A preliminary communication in which the authors announce that the action of bromine on phenylpropiolic acid results in the formation of two isomeric dibromocinnamic acids, which melt at 100° and 139° respectively. The second acid is the more stable of the two, and, like cinnamic acid itself and α-monobromocinnamic acid (m. p. = 131°), is not converted into an indonaphthene-derivative by the action of concentrated sulphuric acid, differing in this respect from the first acid (m. p. = 100°) and from monobromocinnamic acid (m. p. = 120°).

W. P. W.

Polycoumarins. By A. Hantzsch and H. Zürcher (*Ber.*, **20**, 1328—1332).—Pechmann and Duisberg have shown (Abstr., 1884, 66) that when equimolecular proportions of a polyhydric phenol and of ethyl acetoacetate are acted on by a dehydrating agent, methylated hydroxycoumarins are formed. The authors find that if excess of ethyl acetoacetate is employed, small quantities of polycoumarins are formed, as well as the hydroxycoumarins. The reactions are analogous to the formation of polyfurfuran-derivatives described by Lang (this vol., p. 262).

Dimethyldicoumarin, $C_6H_2\left(\begin{matrix}CMe:CH\\O\text{——}CO\end{matrix}>\right)_2$, is formed when a mixture of resorcinol (1 mol.) and ethyl acetoacetate (2 mols. or more) is dissolved in concentrated sulphuric acid, left for some time and then poured into cold water. It is a white, crystalline powder, only very sparingly soluble in alcohol, almost insoluble in boiling water, ether, chloroform, and benzene. It dissolves slowly in ammonia, quickly in the fixed alkalis to a yellow, non-fluorescent liquid. Acids precipitate from this solution *dimethyldicoumaric acid*,

$$C_6H_2(OH)_2 : (CMe : CH\cdot COOH)_2.$$

This acid is a white powder easily soluble in alcohol. In dry air it is slowly, at 140°, rapidly reconverted into the lactone or coumarin. It forms a greenish-blue *copper salt*.

Trimethyltricoumarin, $C_6\left(\begin{matrix}CMe:CH\\O\text{——}CO\end{matrix}>\right)_3$, is formed in a similar way from a mixture of phloroglucol (1 mol.) and ethyl acetoacetate (3 mols.). It is a grey, amorphous powder almost insoluble in the ordinary solvents even on boiling. It dissolves in alkalis, and acids precipitate from this solution *trimethyltricoumaric acid*,

$$C_6(OH)_3(CMe : CH\cdot COOH)_3.$$

This acid resembles the tricoumarin in appearance, and is reconverted into it when heated at 140°. The *sodium salt* forms a granular white powder.

L. T. T.

Tetrachlororthobenzoylbenzoic Acid. By G. KIRCHER (*Annalen*, **238**, 338—349).—*Tetrachlorobenzoylbenzoic acid*, $COPh\cdot C_6Cl_4\cdot COOH$, is prepared by the action of aluminium chloride on tetrachlorophthalic anhydride suspended in benzene. The crude product is poured into water, and the solid mass extracted with boiling water, and afterwards dissolved in aqueous soda. The sodium salt is purified by recrystallisation; on the addition of hydrochloric acid to the solution the free acid is precipitated. It crystallises in needles, and dissolves freely in alcohol, ethyl acetate, and in hot benzene. The acid melts at about 200°. The *sodium salt*, $C_{14}Cl_4H_5O_3Na + 4H_2O$, crystallises in glistening plates. 100 parts of water dissolve 1·7 parts by weight of salt at 20°. $C_{14}Cl_4H_5O_3K + 1\frac{1}{2}H_2O$ is somewhat more soluble in water than the sodium salt. The *copper salts*, $(C_{14}Cl_4H_5O_3)_2Cu + 2H_2O$ and $(C_{14}Cl_4H_5O_3)_2Cu + CuO$, are crystalline compounds insoluble in water. The *methyl salt* crystallises in needles, and melts at 92°. The *ethyl salt* melts at 90°.

At 150° phosphoric chloride converts tetrachlorobenzoylbenzoic acid into the *chloride* $C_6H_5\cdot CO\cdot C_6Cl_4COCl$. This substance crystallises in needles, and melts at 183°. By the action of phosphorus and hydriodic acid on tetrachlorobenzoylbenzoic acid at 180°, *tetrachlororthobenzoylbenzoic acid*, $C_6H_5CH_2\cdot C_6Cl_4\cdot COOH$, is produced. It melts at 156—157°, and dissolves freely in alcohol, benzene, and ether. The *sodium salt*, $C_{14}Cl_4H_7O_2Na + 4H_2O$, forms needle-shaped crystals soluble in water. The crystalline silver salt is sparingly soluble.

Tetrachloranthraquinone, $C_6Cl_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, is formed by dissolving tetrachlorobenzoylbenzoic acid in warm, concentrated sulphuric acid. The solution is poured into shallow basins, and exposed to the atmosphere for several hours. Tetrachloranthraquinone and the sulphonic acid separate out, and are collected on asbestos. On fusion with sodium hydroxide, tetrachloranthraquinone yields phthalic acid, but on oxidation with nitric acid it yields tetrachlorophthalic acid.

Tetrachloranthracene is formed by heating tetrachlorobenzoylbenzoic acid (1 gram) with amorphous phosphorus ($\frac{1}{2}$ gram) and hydriodic acid boiling at 127° ($4\frac{1}{2}$ c.c.) at 220° for five hours. The product melts at 148—149°, and dissolves freely in chloroform, benzene, and carbon bisulphide. It is converted into tetrachloranthraquinone (m. p. 191°) by oxidation with chromic acid. By the action of zinc-dust and dilute ammonia, tetrachloranthracene is converted into *dichloranthracene*. This substance melts at 255°, and is freely soluble in acetic acid, ethyl acetate, and in hot alcohol. When oxidised it yields dichloranthraquinone. This substance forms yellow needles melting at 261°; on fusion with sodium hydroxide, alizarine is produced.

Tetrachloranthraquinonedisulphonic acid, $C_{14}Cl_4O_2H_2(SO_3H)_2$, is freely soluble in alcohol and in water. It forms crystalline barium and calcium salts. W. C. W.

β-Dichlorophthalic Acid. By A. LE ROYER (*Annalen*, **238**, 350—361).—The β-dichlorophthalic acid used in the manufacture of

certain descriptions of eosin melts at 118°, and is freely dissolved by alcohol, ether, chloroform, light petroleum, and hot water. The anhydride melts at 151°. It is soluble in benzene, toluene, and carbon bisulphide. The *ammonium salt*, $C_6Cl_2H_2(COONH_4)_2$, is obtained in white plates by the addition of alcohol and ether to the aqueous solution. The silver salt is crystalline. $C_8H_2Cl_2O_4Ca + 4H_2O$ is sparingly soluble in water, and the barium salt, $C_8H_2Cl_2O_4Ba + 2H_2O$, is still less soluble. *Ethyl dichlorophthalate*, $C_8H_2Cl_2O_4Et_2$, melts at 60°, and forms monoclinic plates; it is soluble in alcohol and ether. The hydrogen salt, $COOH\cdot C_6H_2Cl_2\cdot COOEt$, melts between 75° and 85°. It dissolves in ammonia, forming the compound $COOEt\cdot C_6H_2Cl_2\cdot COONH_4$, which is soluble in water and alcohol.

Dichlorophthalyl chloride, $C_6H_2Cl_2<\begin{matrix}-CO-\\CCl_2\end{matrix}>O$, melts at 50°. The *tetrachloride*, $C_6H_2Cl_2<\begin{matrix}CCl_2\\CCl_2\end{matrix}>O$, melts at 117°. *Dichlorophthalide*, $C_6H_2Cl_2<\begin{matrix}CH_2\\CO-\end{matrix}>O$, melts at 122°, and *dichloro-phthalimide*, $C_8H_3Cl_2O_2N$, melts at 191°.

Orthobenzoyldichlorobenzoic acid, $C_6H_5\cdot CO\cdot C_6H_2Cl_2\cdot COOH$, prepared by the action of aluminium chloride on a solution of dichlorophthalic anhydride in benzene, melts at 159°. It is soluble in alcohol, benzene, and ether. *Toluyldichlorobenzoic acid*, $C_6H_4Me\cdot CO\cdot C_6H_2Cl_2\cdot COOH$, melts at 156°. *Dichlorofluoresceïn* contains 1 mol. H_2O more than ordinary fluoresceïn. It dissolves in alkalis, forming a red solution. *Dichloreosin* forms crystalline potassium and sodium salts, such as $C_{20}H_4O_5Cl_2K_2$.

Tetraiododichlorofluoresceïn, $C_{20}H_8Cl_2I_4O_6$, is prepared by adding iodine to a solution of dichlorofluoresceïn in alkali. It is a reddish-yellow powder. The potassium and sodium salts form the "Rose Bengale" of commerce.

Calcium β-dichlorophthalate yields orthodichlorobenzene on dry distillation. W. C. W.

Tetrachlorophthalic Acid. By C. Graebe (*Annalen*, **238**, 318—338).—*Tetrachlorophthalic acid* melts at 250°, and its anhydride melts at 252° (corr.). 100 parts of water at 14° dissolve 0·57 part by weight of tetrachlorophthalic acid and 0·54 of phthalic acid; at 99°, 3·03 parts of tetrachlorophthalic acid and 18·0 of phthalic acid. Tetrachlorophthalic acid is deposited from aqueous solutions in leaves or plates. It is also freely soluble in alcohol and ether. Tetrachlorophthalic acid is slowly attacked by oxidising agents. Hydriodic acid and phosphorus reduce tetrachlorophthalic acid to *tetrachloroxylylene oxide*, $C_6Cl_4:(CH_2)_2:O$. A solution of tetrachlorophthalic anhydride in glacial acetic acid is reduced to tetrachlorophthalide by zinc-dust. The following salts of tetrachlorophthalic acid have not been previously described. $C_6Cl_4(COOK)_2$ is obtained in anhydrous crystals by adding alcoholic potash to an alcoholic solution of the acid. $C_8Cl_4O_4Ba + 2\frac{1}{2}H_2O$ is a crystalline powder insoluble in water.

$C_8Cl_4O_4Cu + 2H_2O$ is obtained as a crystalline precipitate insoluble in water, by adding copper sulphate to a solution of the ammonium salt. The zinc salt is more soluble in cold than in hot water. It crystallises in needles. The *ethylic salt*, $C_6Cl_4(COOEt)_2$, melts at 60·5°, and the *methyl salt*, $C_6Cl_4(COOMe)_2$, crystallises in prisms which melt at 92°. The acid *ethyl salt*, $COOH{\cdot}C_6Cl_4{\cdot}COOEt$, melts at 94—95°.

Tetrachlorophthalic chloride, $C_6Cl_4{<}^{CCl_2}_{-CO-}{>}O$, crystallises in large prisms. It melts at 118°, and boils at 336°. The *tetrachloride*, $C_6Cl_4{<}^{CCl_2}_{CCl_2}{>}O$, prepared by the action of phosphoric chloride on tetrachlorophthalic anhydride in sealed tubes at 200°, crystallises in rhombohedra. It melts at 140°, and is soluble in ether. *Tetrachlorophthalide* melts at 208·5°. It is soluble in acetic acid and in hot toluene. *Tetrachloroxylylene oxide* melts at 218°. It is deposited from solution in hot benzene or toluene in long needles. When ammonia is passed into the molten anhydride, *tetrachlorophthalimide*, $C_8Cl_4O_2NH$ is formed. It melts at about 360°. *Tetrachlorofluoresceïn* dissolves in a solution of sodium hydroxide. On the addition of an acid, a compound is precipitated which contains one molecule of water more than tetrachlorofluoresceïn. It is *tetrachlororthofluoresceïn*. If ammonia is substituted for sodium hydroxide this compound is not formed.

Tetrachlororthofluoresceïn, $C_{20}Cl_4H_{10}O_6$, is insoluble in water, but soluble in ether. The dilute alkaline solution is distinguished from that of fluoresceïn by its red tint. *Tetrachlorofluoresceïn* is insoluble in ether. The *diacetate* dissolves freely in chloroform. *Tetrachlorogallein*, $C_{20}H_6Cl_4O_7 + 2H_2O$, is formed by the action of pyrogallol on tetrachlorophthalic anhydride at 190°. It is a violet-coloured crystalline powder, and yields a colourless acetic derivative, $C_{20}H_4Cl_4O_7Ac_4$.

W. C. W.

Action of Cyanamide on Benzenesulphonic Acids. By J. Ville (*Compt. rend.*, **104**, 1281—1284).—Amidobenzenesulphonic acid (sulphanilic acid) (10 parts) is heated at 100° in closed tubes for two or three days with water (200 parts), cyanamide (about 3 parts), and 20 to 25 drops of ammonia. The hot, filtered liquid deposits prismatic lamellæ which, when recrystallised, form brilliant needles of the composition $C_7H_9N_3SO_3$. This compound is attacked by sodium hypobromite with evolution of nitrogen, and is decomposed by boiling aqueous solutions of alkalis, with liberation of amidobenzenesulphonic acid, ammonia, and carbonic anhydride. It is therefore a creatine, *α-amidophenylsulphocyamine*, $SO_3H{\cdot}C_6H_4{\cdot}NH{\cdot}C(NH){\cdot}NH_2$. It is neutral, has no odour and no taste, is much less soluble in cold water than sulphanilic acid, is only very slightly soluble in boiling water, and is insoluble in ether. It dissolves to a considerable extent, however, in boiling water. α-Amidophenylsulphocyamine is decomposed by heat with formation of a yellowish-white sublimate. It dissolves in sulphuric and hydrochloric acids without change, and yields no dehydration-product corresponding with creatinine. In this respect it resembles taurocyamine.

With sodium hypobromite it yields a purple-red liquid, and nitrogen is evolved. With nitric acid it forms a colourless solution; with excess of sodium hypochlorite containing a drop of phenol, it gives a fugitive carmine-red coloration. All these reactions serve to distinguish it from sulphanilic acid. C. H. B.

Chlornitro-derivatives of the Aromatic Series. By R. Hirsch (*Ber.*, **20**, 1569—1571).—When amidophenolsulphonic acid suspended in water is treated with bleaching-powder solution a portion goes into solution and the liquid becomes coloured a dull violet, but as soon as sufficient bleaching-powder has been added to bring about the solution of the whole of the acid, a sudden change to a very faint yellow colour occurs. The substance so produced could not, however, be isolated, and treatment of the solution with hydrogen sulphide or zinc-dust failed to effect its reduction to amidophenolsulphonic acid.

Different results are obtained when hydrochloric acid is present, and instead of a violet-coloured intermediate compound being formed quinonechlorimidesulphonic acid is obtained as the chief product of the reaction. This acid also could not be isolated from its golden-yellow solution, but was recognised by various qualitative tests, such as the production of amidophenolsulphonic acid and sulphur by the action of hydrogen sulphide, and of a deep indigo-blue solution on the addition of phenol, α- and β-naphthol, resorcinol, and other phenols, also of dimethylaniline, &c. The blue colour with phenol is ascribed to the formation of a sulphonic acid of indophenol.

The production of chlornitro-derivatives by the action of bleaching-powder on the aromatic amines appears to be a general one, inasmuch as acetanilide chloride (this vol., p. 44), paramidodimethylaniline chloride, and also the chlorides of sulphanilic acid, naphthionic acid, and metamidobenzoic acid have been obtained and recognised by colour reactions. W. P. W.

Sulphimido-compounds. By P. T. Cleve (*Ber.*, **20**, 1534—1538).—*Orthosulphimidobenzene*, $C_6H_4<\overset{NH}{SO_2}>$, is obtained when a solution of orthonitrobenzenesulphonic chloride in benzene is mixed with hydriodic acid diluted with glacial acetic acid. The crystalline product is washed with alcohol and crystallised from boiling glacial acetic acid from which it separates in slender, yellow needles melting at 193°; it is sparingly soluble. *Metasulphimidobenzene*, $C_6H_5NSO_3$, prepared in a manner similar to the ortho-compound, crystallises in yellow needles very readily soluble in boiling alcohol. It melts at 83°. The *para-compound* is an oily substance very readily soluble in glacial acetic acid.

Sulphimidonaphthalene, $C_{10}H_6<\overset{SO_2}{NH}>$ [? $SO_2 : NH = 1 : 4'$], is prepared from α-nitronaphthalenesulphonic chloride, and forms a very sparingly soluble, crystalline powder melting at 167°.

β-Sulphimidonaphthalene, [$NH : SO_2 = 1' : 2$], crystallises in slender,

yellow needles, very sparingly soluble in glacial acetic acid and alcohol. It melts at 180°.

γ-Sulphimidonaphthalene forms lustrous, slender, lemon-coloured needles melting at 124°. It is very sparingly soluble.

δ-Sulphimidonaphthalene resembles its isomerides, and melts at 173°. N. H. M.

Ethyl Benzoic Sulphinide and Ethyl Orthosulphaminebenzoate. By C. Fahlberg and R. List (*Ber.*, **20**, 1596—1604).—*Sodium benzoic sulphinide*, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NNa + 2H_2O$, is formed when pure benzoic sulphinide is exactly neutralised with aqueous soda or sodium carbonate. It crystallises in large, rhombic tables, is extremely soluble in water, sparingly soluble in hot alcohol, and has an intensely sweet taste. If the anhydrous salt is heated with ethyl iodide for some hours at 230°, an almost quantitative yield of *ethyl benzoic sulphinide*, $C_9H_9SO_3N$, is obtained; this crystallises in long, white needles, begins to fuse below its melting point, and melts at 93—94°. It is very readily soluble in alcohol and ether, and, unlike benzoic sulphinide and its salts, is without taste. When heated with hydrochloric acid, the ethyl salt undergoes hydrolysis and yields ethylamine and orthosulphobenzoic acid: a reaction which affords confirmatory evidence in favour of the above formula for the sulphinides.

Potassium orthosulphethamidobenzoate, $COOK\cdot C_6H_4\cdot SO_2NEtK$.—Ethyl benzoic sulphinide is not attacked by boiling with concentrated aqueous potash, but when heated in alcoholic solution with alcoholic potash at 100°, is converted into the potassium salt of orthosulphamidobenzoic acid, which crystallises in nacreous scales, is strongly alkaline, and extremely soluble in water. The *sodium* salt crystallises in tufts of slender needles; the *silver* salt forms aggregates of needles and is soluble in water; the *copper* salt crystallises with 2 mols. of H_2O in dark-green prisms, sparingly soluble in water. The *acid* is obtained as an oil on the addition of an acid to the aqueous solution of the potassium or sodium salts; it crystallises in needles, is soluble in water, readily soluble in alcohol and ether, and has no definite melting point, inasmuch as it begins to fuse at 102°, and is not completely fluid below 116°.

Ethyl orthosulphaminebenzoate, $COOEt\cdot C_6H_4\cdot SO_2NH_2$, is obtained when a solution of benzoic sulphinide in absolute alcohol is saturated with hydrogen chloride. It crystallises in long, white needles, melts at 83°, and is readily soluble in boiling water, alcohol, and ether. On saponification with potash, it yields potassium benzoic sulphinide and alcohol, and similar products are obtained by the action of ammonia, lime, barium hydroxide, and even sodium carbonate in the cold. The ethyl salt is formed if a mixture of ethyl iodide, sodium ethoxide, and orthosulphaminebenzoic acid in molecular proportions is heated for some hours, but cannot be obtained by saturating an alcoholic solution of the acid with hydrogen chloride, inasmuch as in this case benzoic sulphinide is the sole product.

An alcoholic solution of sulphaminebenzoic sulphinide (Abstr.,

1881, 816), when saturated with hydrogen chloride, yields *ethyl disulphaminebenzoate*, $COOEt{\cdot}C_6H_3(SO_2NH_2)_2$, which is converted into the *potassium* salt $NHK{\cdot}SO_2{\cdot}C_6H_3{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NK$, when treated with alcoholic potash, and into sulphaminebenzoic sulphinide with aqueous potash.

W. P. W.

"Saccharin." By E. Maumené (*Bull. Soc. Chim.*, **47**, 92—94).—Fahlberg's "saccharin," as prepared by his patent, is not a definite compound, but is composed of at least two components, which appear to be mixed in equal proportions; neither the mixture nor either of its components agree in composition with the formula given by Fahlberg. A. P.

Indole from Dichlorether and Aniline. By J. Berlinerblau (*Monatsh. Chem.*, **8**, 180—186).—Indole is prepared by heating 50 grams of aniline with an equal volume of water in a reflux apparatus, and gradually adding 25 grams of dichlorether. After being boiled for one hour, the excess of aniline is boiled off, and the residue heated for four to six hours at 210—230°. The indole is obtained by steam distilling.

The formation of indoles from dichlorether and aromatic amines is a general reaction. N. H. M.

Synthesis of Indonaphthene-derivatives. By W. Roser (*Ber.*, **20**, 1574—1576).—*Methylindonaphthenecarboxylic acid*,

$$C_6H_4{<}\begin{matrix}CMe\\CH_2\end{matrix}{>}C{\cdot}COOH,$$

is obtained when ethyl benzylacetoacetate is gently heated with about six times its weight of concentrated sulphuric acid for a short time. It crystallises from alcohol in needles, melts at 200°, and when reduced with sodium amalgam is converted into *methylhydrindonaphthenecarboxylic acid*, $C_6H_4{<}\begin{matrix}CHMe\\-CH_2-\end{matrix}{>}CH{\cdot}COOH$, which melts at 76°.

Methylindonaphthenecarboxylic acid, when suspended in chloroform and treated with bromine (1 mol.), is converted into a bromine-derivative, $C_{10}H_8Br{\cdot}COOH$. This acid crystallises in needles, melts at 245°, and is sparingly soluble in alcohol.

The dihydronaphthoic acid obtained by v. Pechmann (Abstr., 1883, 808) by the action of sulphuric acid on ethyl benzylacetoacetate is most probably identical with methylindonaphthenecarboxylic acid.

W. P. W.

Preparation of Paradinitrodibenzyl. By W. Roser (*Annalen*, **238**, 363—366).—Paradinitrodibenzyl is formed when paranitrobenzyl chloride is treated with a strongly alkaline solution of stannous chloride. W. C. W.

Triphenylmethane-derivatives. By E. Kock (*Ber.*, **20**, 1562—1566).—Attempts to form derivatives of triphenylmethane by the condensation of primary amines of the meta-series and aromatic

aldehydes with or without the addition of zinc chloride, led either to no result or to the formation of resinous products from which crystalline compounds could not be isolated; the substitution of the corresponding hydrochlorides for the bases, or of meta- or para-nitrobenzaldehyde for benzaldehyde produced no difference. When, however, tertiary amines of the meta-series are employed, condensation compounds are readily obtained.

Tetramethdiamidoditolylnitrophenylmethane,

$$NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Me{\cdot}NMe_2)_2,$$

is formed when dimethylmetatoluidine (8 parts) and paranitrobenzaldehyde (5 parts) is heated with zinc chloride and hydrochloric acid at 110° for four hours. It crystallises from a mixture of alcohol and benzene in glistening, golden-yellow scales, and melts at 224°. The *picrate*, $C_{37}H_{35}N_9O_{16}$, forms small, bright-yellow crystals, melts at 199°, and is sparingly soluble in alcohol, ether, benzene, and light petroleum. On reduction, preferably with stannous chloride, the *leuco*-base, $C_{25}H_{31}N_3$, is obtained, and crystallises from alcohol in greyish aggregates melting at 139°. The colour remains unaltered after lengthened exposure to the air, but the alcoholic solution of the base after addition of acetic acid gives with chloranil a wine-red colour quickly changing to a dull-brown. A platinochloride of constant composition could not be obtained.

Tetramethdiamidodichloronitrotriphenylmethane,

$$NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Cl{\cdot}NMe_2)_2,$$

is formed under similar conditions from dimethylmetachloraniline and paranitrobenzaldehyde, and crystallises from benzene in citron-yellow scales melting at 208°. The *picrate*, $C_{35}H_{29}N_9O_{16}Cl_2$, melts at 189°. When reduced with zinc-dust and acetic acid the corresponding *leuco*-base, $C_{23}H_{25}N_3Cl_2$, is obtained, and crystallises from a mixture of alcohol and benzene in almost colourless aggregates melting at 181°. It is unaltered on exposure to the air, yields no coloration on oxidation with chloranil or lead dioxide, and does not form a platinum salt of constant composition.

Metanisidine and paranitrobenzaldehyde readily form a condensation compound without the addition of zinc chloride; the yield, however, is a proportionately small one. The base,

$$NO_2{\cdot}C_6H_4{\cdot}CH[C_6H_3(OMe)NH_2]_2,$$

crystallises from benzene in yellowish-brown scales, melts at 189°, and on reduction yields a readily oxidisable *leuco*-base, which assumes an intense bluish-violet colour on exposure to the air. W. P. W.

γ-Dichloronaphthalene and Monochlorophthalic Acid. By I. Guareschi (*Gazzetta*, **17**, 119—126).—The chlorine atoms in γ-dichloronaphthalene, considering the methods of its formation, must be situated in two different nuclei, both being probably in the α-position. On oxidation with chromic acid in presence of acetic acid, dichloronaphthalene yields a *monochlorophthalic acid*, $C_6H_3Cl(COOH)_2$ [Cl : (COOH)$_2$: O =

1 : 2 : 3], together with a quinone-derivative. The acid crystallises in long, colourless needles, which melt at 184°, and are at the same time converted into the anhydride. When heated with phenol and concentrated sulphuric acid, it yields a phthaleïn, dissolving in potash with violet coloration. The *silver* salt is a crystalline precipitate; the *anhydride* sublimes in colourless needles. This acid is not identical with the monochlorophthalic acids previously described.

The dibromonaphthalene, melting at 130°, yields on oxidation with chromic acid, under conditions similar to those used with the chloro-derivative, a monobromophthalic acid, identical with that obtained by the author in the oxidation of monobromonaphthalene.

V. H. V.

Action of Bromine on Diamido-α-naphthol. By T. Zincke and C. Gerland (*Ber.*, **20**, 1510—1516).—*Bromamido-α-naphthaquinoneimide*, $NH_2{\cdot}C_{10}H_4Br{<}^{-O-}_{NH}{>}$, is formed when the zincochloride of diamidonaphthol (10 grams) is finely rubbed with glacial acetic acid and 5 to 6 c.c. of bromine added. It is washed with glacial acetic acid, stirred with strong ammonia, filtered and crystallised from alcohol. It forms orange-yellow needles which melt at 200·5°, and dissolves readily in hot alcohol and hot benzene; it is insoluble in water. The platinochloride, $(C_{10}H_7BrN_2O)_2,H_2PtCl_6$, crystallises in brown needles.

Bromamido-α-naphthaquinone, $NH_2{\cdot}C_{10}H_4BrO_2$, is obtained by boiling the above imide with much water with repeated additions of sulphuric acid. It crystallises in intensely orange-coloured needles of a silky lustre, which melt at 205° and sublime without decomposition. When boiled with alkali it is converted into bromohydroxyquinone. The *acetyl compound* crystallises in sulphur-coloured plates melting at 136—137°.

Bromohydroxy-α-naphthaquinoneoximide, $OH{\cdot}C_{10}H_4Br{<}^{-O-}_{NH}{>}$, is best prepared by boiling bromamido-α-naphthaquinoneimide with dilute aqueous soda, and adding alcohol from time to time. It is then allowed to settle, and the residue again boiled with soda. It forms deep, brownish-red, slender, lustrous needles, and melts at about 265°; it is sparingly soluble. It does not decompose carbonates. The *sodium salt* crystallises in red needles. The *acetyl-compound* forms hair-like, red needles melting at 270°. The oximide is identical with that formed by the action of ammonia on bromo-β-naphthaquinone.

Bromohydroxy-α-naphthaquinone (Diehl and Merz, *Ber.*, **11**, 1066) is formed when bromamidonaphthaquinone is boiled with dilute alkali, when bromohydroxynaphthaquinoneoximide is boiled with strong hydrochloric acid, and when bromo-β-naphthaquinone is treated with alkali.

N. H. M.

Derivatives of β-Naphthylamine. By L. Maschke (*Chem. Centr.*, 1886, 824).—β-Naphthylamine (6 mols.) when heated with acetic chloride (3 mols.) and phosphorous chloride (1 mol.) at 150° is converted into ethenyl-β-dinaphthylamidine, $C_{10}H_7{\cdot}NH{\cdot}CMe{:}N{\cdot}C_{10}H_7$, melting at 168°. The corresponding benzenyl-derivative, melting at

155°, is prepared in like manner. A mixture of β-naphthylamine (15 grams) and ethylene bromide (3 grams) heated at 150° yields β-ethylenedinaphthylamine, $C_2H_4(C_{10}H_7NH)_2$, which melts at 153°.

Dinitro-β-acetnaphthalide, $C_{10}H_5(NO_2)_2{\cdot}NAc$, is obtained in two isomeric forms, melting at 185° and 235° respectively, by the action of fuming nitric acid on β-acetnaphthalide. These compounds resist the action of reducing agents.

Phthal-β-naphthylimide, $C_{10}H_7N{<}\overset{CO}{CO}{>}C_6H_4$, melting at 218°, is obtained by heating together β-naphthylamine (1 mol.) and phthalic anhydride (1 mol.).

The α-derivative, melting at 182°, is obtained in like manner.

C. F. C.

Substituted Naphthylenediamines. By J. Annaheim (*Ber.*, **20**, 1371—1374).—The author has investigated the action of aniline, &c., on dihydroxynaphthalene.

When dihydroxynaphthalene and aniline are mixed together, some aniline hydrochloride or aqueous hydrochloric acid added, and the whole heated at 160°, *diphenylnaphthylenediamine*, $C_{10}H_6(NHPh)_2$, is obtained. It forms small, glistening crystals soluble in ether, benzene, boiling alcohol, &c. It melts at 163—164° (uncorr.), easily enters into reaction, and when slightly warmed with zinc chloride gives a violet coloration, which disappears on the addition of water.

Paraditolylnaphthylenediamine, $C_{10}H_6(NH{\cdot}C_7H_7)_2$, obtained in like manner from paratoluidine, crystallises in small needles melting at 236—237° (uncorr.). It is almost insoluble in the ordinary solvents, but dissolves in boiling xylene and cumene. It reacts with zinc chloride in the same way as the phenyl-derivative.

L. T. T.

Amidonaphthyl Mercaptans. By A. W. Hofmann (*Ber.*, **20**, 1798—1805).—*Benzenylamido-α-naphthyl mercaptan*, $C_{10}H_6{<}\overset{N}{S}{>}CPh$, is prepared by heating 2 parts of naphthylbenzamide with 1 part of sulphur. The yield is only about 10 per cent. It crystallises in tufts of needles, melts at 100—101°; can be distilled without decomposition at high temperatures, is readily soluble in alcohol and acetic acid, and is practically destitute of basic properties.

Methenylamido-α-naphthyl mercaptan, $C_{10}H_6{<}\overset{N}{S}{>}CH$, prepared in like manner from α-naphthylformamide, is a colourless oil insoluble in water; it distils with steam. The platinochloride,

$$(C_{11}H_7NS)_2,H_2PtCl_6,$$

crystallises in needles.

When α-naphthylacetamide is heated with sulphur, hydrogen sulphide is evolved, *ethenylamido-α-naphthyl mercaptan* distils, whilst the residue consists mainly of the oxalyl-compound. The former resembles the methenyl-compound, but does not distil so readily with steam; its platinochloride, $(C_{12}H_9NS)_2,H_2PtCl_6$, is more soluble, and crystallises in needles.

Oxalyldiamido-α-naphthyl mercaptan, $C_{10}H_6<\begin{matrix}N\\S\end{matrix}>C\cdot C<\begin{matrix}N\\S\end{matrix}>C_{10}H_6$, crystallises in golden-yellow plates, which melt far above 300° with considerable carbonisation; it can be sublimed, but the greater part is always destroyed in the operation. It is scarcely soluble in the ordinary solvents, but can be dissolved in high-boiling petroleum, aniline, or best, nitrobenzene. When fused with potash it yields oxalic acid and *amidonaphthyl mercaptan*, $NH_2\cdot C_{10}H_6\cdot SH$, but from the extreme readiness with which this is converted into the bisulphide it could only be obtained in an impure condition as a viscid oil. The bisulphide is a golden-yellow powder, insoluble in alcohol and ether.

Benzenylamido-α-naphthyl mercaptan crystallises in interlaced needles melting at 107°. Its alcoholic solution shows a green fluorescence. The platinochloride, $(C_{17}H_{11}NS)_2,H_2PtCl_6$, and aurochloride were prepared.

Oxalylamido-α-naphthyl mercaptan forms yellow, crystalline plates, and closely resembles the α-compound. *Amido-β-naphthyl mercaptan* also could only be obtained in admixture with the bisulphide.

A. J. G.

Naphthoic Acids. By Å. G. Ekstrand (*Ber.*, **20**, 1353—1361).—The dinitro-α-naphthoic acid (m. p. 265°), previously described (this vol., p. 373, and Abstr., 1886, 948), when reduced with tin and hydrochloric acid yields, Aguiar's diamido-acid, obtained from the so-called β-dinitronaphthalene, which the author showed (Abstr., 1886, 155) to be the α-α-compound. This naphthoic acid must therefore have the constitution [$NO_2 : NO_2 : COOH = 1 : 1' : 4$].

α-Mononaphthoylhydroxamic acid, $C_{10}H_7\cdot CO\cdot NH\cdot OH$, is formed by the reaction of equal molecular proportions of hydroxylamine and α-naphthoic chloride. It crystallises in glistening scales, soluble in boiling water, almost insoluble in alcohol, and melts at 186—187°. It forms a potassium salt, but this decomposes very readily with formation of α-naphthylamine. When treated with β-naphthoic chloride the above acid yields α-α-dinaphthyl-carbamide. Together with the above mono-acid, *α-α-dinaphthoylhydroxamic acid*, $OH\cdot N(CO\cdot C_{10}H_7)_2$, is always formed. This crystallises in needles melting at 150°, and soluble in boiling alcohol. Its *potassium salt* crystallises in needles soluble in alcohol.

β-Mononaphthoylhydroxamic acid, prepared from β-naphthoic chloride, forms small, quadratic scales, easily soluble in alcohol, and melting at 168°. *β-β-Dinaphthoylhydroxamic acid* yields small needles melting at 171°. The *potassium salts* of both acids are crystalline. *β-β-Dinaphthoylcarbamide* crystallises in needles melting at 286°.

α-β-Dinaphthoylhydroxamic acid is obtained by heating the β-mono-derivative with α-naphthoic chloride at 100°. It crystallises from boiling alcohol in needles melting at 160°.

L. T. T.

Action of Sodium on Alcoholic β-Naphthonitrile. By E. Bamberger and O. Boekmann (*Ber.*, **20**, 1711—1712).—*Tetrahydro-β-naphthobenzylamine*, $C_{10}H_{11}\cdot CH_2\cdot NH_2$, is obtained by gradually adding 10 grams of sodium to a hot solution of 10 grams of β-naphthonitrile

in 100 grams of alcohol. It is a colourless liquid of odour closely resembling that of the α-compound (this vol., p. 719), boils at 270·2° (corr.) under 729 mm. pressure, and does not fluoresce when pure. It is a strong non-acid base, which absorbs carbonic anhydride from the air. The hydrochloride, $C_{11}H_{16}NCl$, crystallises in tufts of needles and melts at 228·5—229°; the platinochloride, $(C_{11}H_{16}NCl)_2PtCl_4$, forms small, lustrous, yellow needles; the sulphate crystallises in long, lustrous, thin prisms. The bye-products of the reaction are dihydronaphthalene, identical with that obtained from the α-compound (*loc. cit.*), ammonia, hydrogen cyanide, β-naphthoic acid, and frequently β-naphthamide. Of these, the first alone occurs in any considerable quantity. A. J. G.

Trimethylnaphthalene. By L. Maschke (*Chem. Centr.*, 1886, 824).—β-Naphthylamine was heated with methyl iodide and methyl alcohol at 100°, and the resulting ammonium iodide heated for some hours at 300—335°. From the resinous product, the hydrocarbon was isolated by distillation with steam. It boils at 275°, and yields a well defined picrate melting at 132—133°. C. F. C.

2 : 3 Dimethylanthraquinone. By K. Elbs and H. Eurich (*Ber.*, **20**, 1361—1363).—2 : 3 *Dimethylanthraquinone* was obtained by heating F. Meyer's orthoxylenephthaloic acid,

$$C_6H_3Me_2\cdot CO\cdot C_6H_4\cdot COOH,$$

(Abstr., 1882, 848). It is best crystallised from xylene, and melts at 183°. It resembles anthraquinone in properties. When heated with nitric acid (sp. gr. 1·1) at 210—220° it yields 2 : 3 *anthraquinonedicarboxylic acid;* this crystallises in yellow needles, is sparingly soluble in the usual solvents, and melts at 340°. It dissolves in ammonia to a red solution, which, however, cannot be evaporated without decomposition. Its salts all have a reddish colour. When treated with water it is converted into yellow needles of the *anhydride* which melt at 290°. The ammoniacal solution is reduced by zinc-dust to 2 : 3 *anthracenedicarboxylic acid*, which forms a crystalline powder melting at 345°. The quinone yields with ammonia and zinc-dust 2 : 3 *dimethylanthracene* melting at 246°. The *picrate* forms unstable, red needles. L. T. T.

1 : 3 Dimethylanthraquinone. By K. Elbs and M. Günther (*Ber.*, **20**, 1364—1367).—This compound has already been briefly described by Elbs (Abstr., 1886, 557). When oxidised with dilute nitric acid it yields 1 : 3 *anthraquinonedicarboxylic acid*, which is sparingly soluble in the usual solvents, crystallises in needles, and is still solid at 330°. When reduced with zinc-dust in ammoniacal solution, this acid yields 1 : 3 *anthracenedicarboxylic acid.* This is a crystalline powder, sparingly soluble in the usual solvents, and still solid at 330°. When the quinone is reduced with zinc-dust in ammoniacal solution no dimethylanthracene is formed, but a compound of the composition $C_{16}H_{12}$ is obtained; this is readily soluble in boiling alcohol, crystallises in scales, and melts at 85°. It

forms a compound with picric acid, crystallising in brownish-red scales melting at 135°. Chromic acid in acetic solution reconverts it into the quinone. Its constitution is not yet definitely settled.

L. T. T.

Derivatives of Camphor. By L. Balbiano (*Gazzetta*, **17**, 95—99).—When bromocamphor is heated with phenylhydrazine it yields camphyldiphenyldehydrazine, $N_2PhH_2{\cdot}C_{10}H_{15}$: N_2HPh.

Four monochlorocamphors have been described; it is here shown that one of the physically isomeric chlorocamphors obtained by Cazeneuve by the direct chlorination of camphor, is identical with that obtained by Schiff and Puliti by the decomposition of chlorocamphor-carboxylic acid. This compound, which melts at 92—92·5°, when heated with phenylhydrazine yields a camphyldiphenyldehydrazine, melting at 55—56°, and identical with that obtained from bromocamphor. The other physical isomeride, melting at 100·5°, but softening at 94·5°, yields under similar conditions the same phenylhydrazine-derivative. These experiments further confirm the view that camphor contains the ketonic group.

V. H. V.

Isomeric Mononitro-camphors. By P. Cazeneuve (*Compt. rend.*, **104**, 1522—1525).—600 grams of granulated zinc is treated with 1000 c.c. of a 10 per cent. solution of copper sulphate, and when the copper is deposited, the metal is washed and mixed with 1500 grams of alcohol of 93° and 300 grams of the chloronitrocamphors obtained by the action of fuming nitric acid on monochlorcamphor. The mixture is heated to boiling for five minutes, and the alcohol decanted off in order to stop the reaction. When the brown liquid has cooled, it is mixed with zinc-dust, filtered, concentrated to two-thirds, mixed with a warm concentrated solution of 120 grams of sodium carbonate, heated with agitation, diluted with 2000 c.c. of water, boiled with animal charcoal, and filtered. The nitrocamphors are precipitated by adding hydrochloric acid, and the precipitate is treated with cold alcohol of 60°, which dissolves the β-nitrocamphor, but leaves the α-derivative undissolved.

The *α-nitrocamphor* is crystallised from boiling alcohol of 93°, and then from benzene. It forms large, rhombic prisms, insoluble in water but soluble in strong alcohol, and very soluble in benzene. It melts at 100—101°, and decomposes at 160°; it burns quietly on platinum foil, and does not detonate when rapidly heated. Its solution in benzene is lævogyrate, the rotatory power diminishing as the concentration increases. α-Nitrocamphor reddens litmus and decomposes carbonates, forming well-defined salts. An alcoholic solution of the copper salt is maroon-coloured, of the ferrous salt garnet-red, of the ferric salt blood-red. The quinine salt crystallises readily with alcohol. α-Nitrocamphor forms ethereal salts. It is not affected by concentrated potash or soda, but when heated with water in sealed tubes it yields ammonia and nitric acid. With a mixture of sulphuric acid and fuming nitric acid it seems to form a dinitro-derivative, which is decomposed by water with evolution of nitric oxide and formation of camphoric anhydride.

β-Nitrocamphor crystallises with difficulty in microscopic, arborescent

forms. It is very soluble in dilute alcohol and in benzene, the alcoholic solution being dextrogyrate, whilst the benzene solution is feebly lævogyrate. It alters readily and becomes yellow when heated. It is decomposed by boiling alkalis, and its salts are much more soluble than those of the α-derivative.

Another isomeride exists, and will be described in a subsequent paper. C. H. B.

Anemonin. By Hanriot (*Compt. rend.*, **104**, 1284—1286).—Anemonin was obtained by Heyer from various species of anemones. The author prepared it by distilling *Anemone pulsatilla* in a current of steam until the distillate no longer gave a yellow coloration with potash. The distillate was redistilled and allowed to remain in a cool place for several months, when it deposited the anemonin, which was purified by solution in alcohol and recrystallisation from benzene, from which it separates in slender needles of the composition $C_{15}H_{12}O_6$. A product is also obtained which has practically the same composition, but is insoluble in alcohol.

Anemonin melts at 156°, and decomposes at 270° with partial sublimation of anemonin and a liquid which appears to be an aldehyde. With zinc-dust or with hydriodic acid in sealed tubes, it gives no distinct reaction, but a small quantity of a hydrocarbon is formed which seems to be cymene or cumene.

If anemonin is dissolved in chloroform and treated with excess of bromine it yields the compound $C_{15}H_{12}O_6Br_4$; this crystallises from benzene in octahedra which do not melt without decomposition.

When treated with nascent hydrogen in an acid solution anemonin yields hydroanemonin, $C_{15}H_{20}O_6$, which crystallises from boiling petroleum in large, colourless lamellæ which contain 1 mol. H_2O, melt at 78°, and distil without decomposition at 210—212° under a pressure of 10 mm. Hydroanemonin is much more stable than anemonin. It is insoluble in cold solutions of the alkalis, yields no derivative with acetic anhydride, and no chlorine-derivative with phosphorus pentachloride. The latter reagent only partially converts it into anemonin. C. H. B.

Action of Acetic Anhydride on Methylpyrroline and Benzylpyrroline. By G. Ciamician and P. Silber (*Ber.*, **20**, 1368—1370).—Ciamician and Dennstedt have already described (Abstr., 1885, 378) a monacetyl-derivative of methylpyrroline. By using a very large excess of anhydride and heating for eight hours at 250°, the authors have obtained *diacetomethylpyrroline*, $C_4NH_2MeAc_2$. This crystallises in colourless needles melting at 133—134°, and is easily soluble in ether, alcohol, benzene, chloroform, and boiling water.

The authors obtained a *benzylpyrroline* by heating the potassium compound of pyrroline with benzyl chloride. It is solid at ordinary temperatures, but melts with the warmth of the hand to a colourless liquid which boils at 247° (uncorr.). It is almost insoluble in water, easily soluble in alcohol and ether. When heated at 240° for some hours with a large excess of acetic anhydride, it yields *diaceto-benzylpyrroline*, $C_7H_7{\cdot}C_4NH_2Ac_2$, which crystallises in colourless needles, is soluble in alcohol, and melts at 129—130°. L. T. T.

Action of Propionic Anhydride on Pyrroline. By M. Dennstedt and J. Zimmermann (*Ber.*, **20**, 1760—1762).—It has been shown that two isomeric acetyl-derivatives are obtained by the action of acetic anhydride on pyrroline; a similar result is obtained by heating pyrroline with propionic anhydride and sodium propionate in a reflux apparatus, when two propionylpyrrolines are obtained, of which one only distils with steam. The yield is not good.

Propionylpyrroline, $C_4NH_4{\cdot}COEt$ [COEt = 1], is a viscid, yellowish oil which distils at 192—194°, can also be distilled with steam, and is decomposed by alkalis into pyrroline and propionic acid.

The isomeric propionylpyrroline, [COEt = 2 or 3], crystallises in colourless needles, melts at 52°, boils at 222—225°, is soluble in alkalis without decomposition, and yields a white, crystalline silver-derivative, $C_4NH_3Ag{\cdot}COEt$ [Ag : COEt = 1 : 2 or 3].

Dipropionylpyrroline, $C_4NH_3(COEt)_2$, obtained by heating 5 grams of pyrroline with 50 grams of propionic anhydride at 260°, crystallises in colourless plates, and melts at 126—117°. A. J. G.

Preparation of Halogen-derivatives of Pyridine Bases from the Pyridinecarboxylic Acids. By G. Pfeiffer (*Ber.*, **20**, 1343—1353).—It is well known that the pyridine bases are very indifferent towards substitution-reagents, and very few substitution-products are at present known. The author finds that halogen substitution-products may easily be made through the mediation of the carboxylic acids.

Bromine does not act on collidinedicarboxylic acid in either alkaline or acid solution, but when added to a neutral solution of the potassium salt, carbonic anhydride is evolved and *symmetrical dibromocollidine*, $CMe\langle^{CBr{\cdot}CMe}_{CBr:CMe}\rangle N$, is obtained. This forms snow-white, nacreous crystals soluble in alcohol and ether, almost insoluble in water. It melts at 81° and boils at 262—263° under a pressure of 726 mm. and volatilises slowly even at ordinary temperatures. It is a feeble base, dissolves in hot concentrated hydrochloric acid, and the solution on cooling deposits small, polyhedric crystals of the *hydrochloride* $C_8NH_9Br_2,HCl$. This is easily soluble in water, and the aqueous solution decomposes on boiling. The dry substance sublimes slightly when rapidly heated, but decomposes into its components even at 100°, very rapidly at about 200°. With bromine it yields a dibromide, $C_8NH_9Br_2,Br_2HCl$. The *platinochloride* forms orange needles containing 2 mols. H_2O which it loses at 120°: the *dichromate* melts at 146°; the *picrate* at 159—160°; the *aurochloride* forms yellow needles. When oxidised with permanganate the base yields *dibromopyridinetricarboxylic acid*, $C_5NBr_2(COOH)_3$, crystallising in needles soluble in boiling water, sparingly so in alcohol and ether. It melts with decomposition at 204—206°. The *monopotassium salt*,

$$COOK{\cdot}C_5NBr_2(COOH)_2 + 6H_2O,$$

forms colourless needles soluble in hot water. This salt is not decomposed by mineral acids, and the free acid is best obtained from the *silver salt*, $C_5NBr_2(COOAg)_3$, which forms an insoluble, crystalline powder. Ferrous sulphate gives a carmine coloration. When heated

in glacial acetic solution no decomposition takes place; when the acid is heated alone all three carboxyl-groups are eliminated and Hofmann's 3 : 5 dibromopyridine formed. When dibromocollidine is heated with sodium ethoxide, 3 : 5 *diethoxycollidine*, $C_5NMe_3(OEt)_2$, is formed; it boils at 217—219° under 726 mm. pressure.

Symmetrical potassium lutidine dicarboxylate yields with bromine *dibromolutidine*, $C_5NHMe_2Br_2$. It very closely resembles dibromocollidine in appearance, and melts at 65°.

Quinolinic acid when treated with bromine under like conditions yields 3 : 5 dibromopyridine, and the same compound was formed by the action of bromine on pyridinepentacarboxylic acid.

When quinolinic acid in slightly alkaline solution is treated with iodine, *diiodohydroxypyridine*, $C_5NH_2I_2(OH)$ [OH : I : I = 2 : 3 : 5], is formed. This forms light-brown needles sparingly soluble in alcohol, ether, and boiling water (the latter solution having an acid reaction) and melting at 257—259°. When heated very carefully it sublimes in colourless needles, but decomposes if heated rapidly. It dissolves in moderately strong sulphuric acid, but is reprecipitated unchanged on the addition of water. Its acid character is more marked, the *sodium compound* crystallising with $3H_2O$ in colourless scales. It also forms well-marked compounds with many other metals. L. T. T.

Action of Chloral on α-Picoline. By A. Einhorn and A. Liebrecht (*Ber.*, **20**, 1592—1594).—When equimolecular proportions of α-picoline and chloral are mixed together, rise of temperature occurs, and a white, crystalline mass is obtained which yields *ω-trichloro-α-hydroxypropylpyridine*, $C_5NH_4{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, if it is heated for 8 to 10 hours either with or without zinc chloride. This compound crystallises from dilute alcohol in beautiful, six-sided tables, melts at 86—87°, and yields well-characterised salts with acids. The *hydrochloride*, $C_8H_8NOCl_3,HCl$, crystallises in compact, long needles, melts at 201—202°, and is soluble in absolute alcohol. When heated with alcoholic potash, the base is converted into α-pyridylacrylic acid, which forms a white, crystalline *hydrochloride*, $C_8H_7NO_2,HCl$, melting at 220° with decomposition. W. P. W.

Behaviour of the Nitrobenzaldehydes towards Ethyl Acetoacetate and Ammonia. By R. Lepetit (*Ber.*, **20**, 1338—1343).—The author has investigated the action of ammonia and ethyl acetoacetate on the three isomeric nitrobenzaldehydes. When metanitrobenzaldehyde (1 mol.), ethyl acetoacetate (2 mols.), and a slight excess of ammonia are heated in alcoholic solution, *ethyl metanitrophenyllutidinehydrodicarboxylate*, $NO_2{\cdot}C_6H_4{\cdot}C_5NH_2Me_2(COOEt)_2$, is formed. It is easily soluble in alcohol, ether, chloroform, and acetone, crystallises in plates, and melts at 161°. When a small quantity of fuming nitric acid is added to an alcoholic solution and a current of nitrous acid then passed in, *ethyl metanitrophenyllutidinedicarboxylate*,

$$NO_2{\cdot}C_6H_4{\cdot}C_5NMe_2(COOEt)_2,$$

is produced. It crystallises in colourless plates, soluble in ether and alcohol, and melting at 65°. The *nitrate* forms colourless, acicular

crystals melting at 129—130°; the *platinochloride*, orange crystals melting at 202°. When treated with tin and hydrochloric acid the ethyl salt yields *ethyl metamidophenyllutidinedicarboxylate*, which is soluble in alcohol and ether, crystallises in plates, and melts at 109—110°. This compound is bibasic, and forms a *platinochloride*,

$$C_{19}H_{22}N_2O_4,H_2PtCl_6 + H_2O,$$

which crystallises in yellow needles, loses water at 110—120°, and decomposes at about 260° without previous fusion. This amido-compound acts as a primary aromatic amine, and may be diazotised, &c.

Paranitrobenzaldehyde reacts in a similar way, but the reaction does not take place so smoothly, a great deal of secondary products and resinous matter are formed, and the yield is very small. The hydro-compound was not obtained quite pure, but is crystalline and melts at about 118—122°.

With orthonitrobenzaldehyde the reaction takes place differently. A substance, $C_{19}H_{20}N_4O_5$, is always formed as well as the hydro-salt, and the yield of these two substances appears to be better when equimolecular proportions of ethyl acetoacetate and nitrobenzaldehyde are taken than when the usual proportion 2 : 1 is employed. *Ethyl orthonitrophenyllutidinehydrodicarboxylate* forms pale-yellow, rhombic plates, is soluble in alcohol and ether, and melts at 119—120°. It is insoluble in dilute acids. When oxidised with nitrous acid so little crystallisable substance was obtained that the non-hydrogenised compound could not be obtained in a pure state. The compound, $C_{19}H_{20}N_4O_5$ (possibly $C_{19}H_{22}N_4O_5$), mentioned above is very sparingly soluble in alcohol, crystallises in yellow needles, and melts at 189°: it has basic properties. The *hydrochloride*, $C_{19}H_{21}N_4O_5Cl$, forms a sparingly soluble, yellow powder, loses hydrogen chloride in dry air, rapidly at 100°, and melts with partial decomposition at 150°; it also forms a *platinochloride*. This compound is unstable, and, when it is boiled with hydrochloric acid, ethyl chloride and carbonic anhydride are evolved, whilst orthonitrobenzaldehyde is amongst the residual products. Attempts at hydrolysis and reduction were unsuccessful. When nitrous acid is passed through alcohol in which the base is suspended, solution takes place, and, after a time, white needles separate which have the same composition, $C_{19}H_{20}N_4O_5$, as the base, but are non-basic in character, and decompose at 192°.

With phenylhydrazine all three nitrobenzaldehydes react in the usual way with formation of hydrazides of the constitution $NO_2{\cdot}C_6H_4{\cdot}CH : N_2HPh$. The *ortho-compound* forms small, ruby-red prisms melting at 152°; the *para-compound* dark-red crystals, with a bluish surface fluorescence, and melting at 155°; and the *meta-compound* scarlet crystals melting at 120°. L. T. T.

Cinchonic Acid. By A. Claus and M. Kickelhayn (*Ber.*, **20**, 1604—1606).—Whilst engaged in the preparation of a large quantity of cinchonic acid, obtained by the oxidation of 6 kilos. of cinchonine with nitric acid, the authors have observed that it crystallises in three forms: 1, in the well-known, slender, caffeïne-like needles with

1 mol. of H_2O; 2, with 2 mols. of H_2O in the triclinic forms described by Muthmann and Nef (this vol., p. 598); and, 3, in monoclinic tables also with 2 mols. of H_2O. The first form is always obtained when the hot, concentrated solution of the acid is allowed to cool during crystallisation; the third form separates during the slow evaporation of dilute aqueous solutions of the pure acid; whilst the second form, according to the authors' experience, is got by the slow crystallisation of solutions of the acid containing some impurity such as mineral acid, and, after repeated recrystallisation, yields the third form on the slow evaporation of its dilute aqueous solution.

The crystallographic measurements of the third form agree with those of Ditscheiner (*Annalen*, **173**, 84), and, consequently, Muthmann and Nef's conclusions cannot be maintained. The crystals are monoclinic, $a : b : c = 0{\cdot}2758 : 1 : 0{\cdot}5328$; $\beta = 98° 3'$; and the following faces were observed: $\infty\breve{P}\infty$, ∞P, $\breve{P}\infty$, and $\frac{1}{3}\breve{P}\infty$. W. P. W.

Synthesis of Quinoline-derivatives. By L. Knorr (*Ber.*, **20**, 1397—1399).—When ethyl β-phenylamido-α-crotonate is heated at 190—200° it yields γ-hydroxy-quinaldine described by Conrad. By the action of dry sodium ethylate on the crotonate the author obtained a compound, $C_{14}H_{13}NO_3$, which appears to be Conrad and Limpach's phenyllutidoncarboxylic acid. L. T. T.

Reactions of Quinoline. By H. Weidel (*Monatsh. Chem.*, **8**, 120—146).—When a mixture of dry quinoline hydrochloride (from 50 grams of quinoline), 50 grams of quinoline, and 10 grams of platinised asbestos, is heated at 170°, and subsequently at 200°, in a gentle current of dry oxygen, the whole becomes dark in colour and thick. It is then dissolved in dilute hydrochloric acid, filtered, and treated with alkali and steam-distilled. The residue is dissolved in very dilute hydrochloric acid, and fractionally precipitated with a concentrated solution of sodium acetate. The last precipitate yielded on further purification dichinolyl, melting at 173°. The yield is 8 per cent.

When quinoline hydrochloride (from 129 grams of base), 93 dry pure aniline, and 25 grams of platinised asbestos are heated together, first at 160°, then for some hours at 175°, and finally at 180°, paramido-α-phenylquinoline (Jellinek, Abstr., 1886, 1045) and a new diquinolyl are obtained. This melts at 138° (uncorr.). It yields two hydrochlorides; the one (with 2 mols. HCl) is colourless, the other (with 1 mol. HCl) yellow. The yield of base is 25 to 40 per cent. of that required by theory. The *acetyl-derivative*, $C_{15}H_{11}N_2Ac$, crystallises from alcohol in lustrous plates, melting at 189° (uncorr.).

Dihydroxyphenylquinoline, $C_{15}H_{11}NO_2$, is obtained, together with parahydroxy-α-phenylquinoline, by the action of potassium nitrite on amido-α-phenylquinoline, in presence of excess of hydrochloric acid. It crystallises in colourless, lustrous, prismatic needles, insoluble in water, readily soluble in benzene, ether, alcohol, chloroform, and acetone; it melts at 114° (uncorr.).

Parahydroxy-α-phenylquinoline, $C_{15}H_{11}NO$, forms a loose mass of colourless, slender, monoclinic crystals, insoluble in water, readily

soluble in boiling benzene, xylene, and alcohol, in hydrochloric acid, and in aqueous potash. It melts at 237—238° (uncorr.), and distils without decomposition under 62 mm. pressure. The *hydrochloride* (with 2 mols. H_2O) crystallises in hair-like crystals of a lemon-yellow colour; the *platinochloride*, $(C_{15}H_{11}NO)_2,H_2PtCl_6$, crystallises in gold-coloured, thin plates. The *acetyl-derivative* crystallises in large, colourless, thin, rhombic plates, melting at 123°; it is readily soluble in ether, benzene, and ethyl acetate. When hydroxyphenylquinoline is oxidised with chromic acid, quinaldic acid melting at 157° is formed; when distilled with zinc-dust it is almost quantitatively converted into α-phenylquinoline. By the action of tin and hydrochloric acid on hydroxy-α-phenylquinoline, *tetrahydrohydroxy-α-phenylquinoline*, $C_{15}H_{15}NO$, is formed: this could not be obtained in crystals. The *hydrochloride* forms white, lustrous, prismatic crystals. The solution gives with ferric chloride an intense blood-red coloration; with nitric acid first a red-violet, then a brown-red colour is produced. When fused with potash, parahydroxybenzoic acid is formed. The above reactions point to the following constitutional formula for paramido-α-phenylquinoline:—

$$C_9NH_6{\cdot}C_6H_4{\cdot}NH_2\ [C_6H_4{\cdot}NH_2 = 2';\ C_9NH_6 : NH_2 = 1 : 4].$$

The *nitro-derivative* of parahydroxy-α-phenylquinoline, $C_{15}H_{10}N_2O_3$, was also obtained in the product of the action of potassium nitrite and hydrochloric acid on paramido-α-phenylquinoline. It crystallises in microscopic lemon-yellow plates, melting at 151°; it is rather readily soluble in alcohol and ether.

Diquinolyl, $C_{18}H_{12}N_2$, is contained in the mother-liquor from the preparation of paramido-α-phenylquinoline. It is best prepared by heating a mixture of 20 grams of paramido-α-phenylquinoline, 20 grams of glycerol, 40 grams of sulphuric acid, and 5 grams of nitrobenzene, at 180°, until frothing ceases. The product is dissolved in water, filtered, neutralised with sodium carbonate, and repeatedly extracted with ether. The residue obtained by evaporating off the ether is converted into the hydrochloride, which is recrystallised several times. The free base crystallises from alcohol (by slow evaporation) in monoclinic crystals of a fatty lustre: $a : b : c = 1{\cdot}3685 : 1 : 2{\cdot}3778$. It melts at 144° (uncorr.), is readily soluble in benzene, xylene, and alcohol, less in ether. It volatilises without decomposition. The *platinochloride*, $C_{18}H_{12}N_2,H_2PtCl_6$, forms a yellowish-white, microcrystalline powder, almost insoluble in water. The *methiodide*, $C_{18}H_{12}N_2,MeI + H_2O$, crystallises in small, bright yellow needles, melting at 231—232°, very sparingly soluble. The *monosulphonic acid* prepared by heating diquinolyl with 5 parts of sulphuric acid at 160—180°, forms a white, chalky powder, soluble in dilute alkali solutions. When the sulphuric acid is heated with potash at 220°, *hydroxydiquinolyl*, $C_{18}H_{12}N_2O$, is formed. This forms a crystalline powder, readily soluble in boiling benzene and alcohol; it melts at 187°. N. H. M.

Action of Acetamide on Orthochloroquinoline. By F. Muhlert (*Ber.*, **20**, 1551—1552).—When chloroquinoline is heated

for several hours with acetamide, carbostyril is formed; the latter is also obtained together with benzonitrile when benzamide is used instead of acetamide. N. H. M.

Quinoline-derivatives from β-Diketones. By C. Beyer (*Ber.*, **20**, 1767—1773).—In the method for the preparation of quinoline-derivatives from aromatic amines and the condensation-products obtained by the action of hydrogen chloride on mixtures of fatty aldehydes with certain ketones (Abstr., 1886, 629), it seemed probable that an anilide is first formed, and is converted into the quinoline-derivative in the further course of the reaction. Proof of the truth of this idea is given in the present paper.

Benzoylacetoneanilide,

$$COPh{\cdot}CH_2{\cdot}CMe : NPh, \text{ or } COPh{\cdot}CH : CMe{\cdot}NHPh,$$

is prepared by heating aniline and benzoylacetone in equimolecular proportions at 150°, or by boiling the mixture with glacial acetic acid in a reflux apparatus for some hours. It crystallises in yellowish-white plates, and melts at 110°. When heated with concentrated sulphuric acid the anilide is converted into γ-phenylquinaldine.

Dibenzoylmethane, $CH_2(COPh)_2$, under like treatment also yields an anilide; this could not be obtained in a state of purity, but the crude product when heated with sulphuric acid yields 2 : 4-*diphenylquinoline*, $C_9NH_5Ph_2$. This forms a white, crystalline mass, melts at 112°, and shows feebly basic properties, its sulphate dissociating readily when treated with pure water. The sulphate, chromate, and platinochloride, $(C_{21}H_{15}N)_2,H_2PtCl_6 + 2H_2O$, were prepared.

A. J. G.

Acridaldehyde and Acridinecarboxylic Acid. By A. Bernthsen and F. Muhlert (*Ber.*, **20**, 1541—1551).—*Methyl acridinechloral*, $C_{13}H_8N{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, is prepared by adding 70 grams of chloral to 60 grams of methylacridine suspended in 600 grams of benzene. The temperature is raised to 70—75°, when the methylacridine is completely dissolved, and a separation of a yellow, sandy precipitate takes place. After some hours it is filtered, washed, and extracted with boiling alcohol or benzene. The yield is almost equal to that required by theory. It is sparingly soluble in alcohol, and crystallises in needles or prisms which melt with decomposition above 200°. It is almost insoluble in dilute acids, and dissolves in strong sulphuric acid without decomposition, yielding a splendid, fluorescent solution.

Acridylacrylic acid, $C_{13}H_8N{\cdot}CH : CH{\cdot}COOH$, is obtained by saponifying the above chloral-compound with an excess of 20 per cent. aqueous soda, mixed with half its volume of alcohol. It forms an almost insoluble, crystalline powder, which decomposes when heated at 208°, with evolution of carbonic anhydride. It has acid as well as basic properties. The solutions of the alkali salts show a green fluorescence. The *potassium salt* forms slender needles very readily soluble; the *sodium*, *ammonium*, and *silver salts* are described. The *hydrochloride* crystallises in well-formed, flat needles. When

this is reduced, *hydroacridylacrylic acid*, $C_{13}H_{10}N\cdot CH\cdot CH:CH\cdot COOH$, is obtained. This is readily soluble in alcohol and ether, sparingly in water. The *sodium salt* forms flat needles very readily soluble.

Acridaldehyde, $C_{13}H_8N\cdot CHO$, is prepared by dissolving 15 grams of acridylacrylic acid in excess of sodium carbonate solution, diluting to 750 c.c., adding 500 c.c. of benzene, cooling the whole to 0°, and shaking vigorously with a not too concentrated solution of 15 grams of potassium permanganate. After some time it is filtered through calico, the aqueous solution separated and extracted with ether. The united benzene and ether extracts are extracted with dilute hydrochloric acid. It crystallises from hot alcohol in slender, yellow needles of a silky lustre, melts at 139—140°, and boils with partial decomposition at a higher temperature. The *hydrochloride* forms gold-coloured, slender needles, which are decomposed by warm water; the *nitrate* crystallises in slender, yellow needles less soluble than the hydrochloride; the *sulphate* forms sparingly soluble, gold-coloured, lustrous needles; the *chromate* forms short, slender prisms. The *phenylhydrazine-compound*, $C_{20}H_{15}N_3$, crystallises from alcohol in hexagonal plates, insoluble in water; the *salts* form microscopic violet needles of a green metallic lustre, sparingly soluble in water, more soluble in alcohol; the solutions are violet-blue.

Acridinecarboxylic acid, $C_{13}H_8N\cdot COOH$, is obtained by adding the finely-powdered aldehyde to a warm 5 per cent. sodium hydroxide solution containing an excess of freshly precipitated silver oxide. It crystallises in lustrous, yellow needles, soluble in alcohol, less soluble in water. When heated at 300° it is decomposed into acridine and carbonic anhydride. The *sodium* and *ammonium salts* are readily soluble; salts with acids do not appear to be capable of existing. When the solutions of the alkali salts are diluted they show a blue fluorescence. N. H. M.

Creatines and Creatinines: α-Amidocaprocyamine and α-Amidocaprocyamidine. By E. Duvillier (*Compt. rend.*, **104**, 1290—1292).—*α-Amidocaprocyamine* is obtained by mixing an aqueous solution of leucine with at least 2 parts of cyanamide and a few drops of ammonia, and allowing the liquid to remain for several months. The liquid is then evaporated to dryness, repeatedly extracted with alcohol to remove dicyanamide, and the insoluble residue crystallised from water, from which it separates in anhydrous lamellæ of the composition $NH:C(NH_2)\cdot NH\cdot CH(COOH)\cdot CH_2\cdot CH_2\cdot CH_2Me$. It is very slightly soluble in cold water, more soluble in hot water, very slightly soluble in alcohol.

α-Amidocaprocyamidine is obtained by boiling the preceding compound in water for several hours. It crystallises in needles, which are very slightly soluble in cold alcohol, but dissolve more readily in hot alcohol, and are about as soluble in water as the preceding compound. From hot water it crystallises in silky, anhydrous needles. It has the composition $<\begin{matrix}NH\text{——}CO\\C(NH)\cdot NH\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CH_2Me$, and when boiled with water is reconverted into the corresponding cyamine.

It is worthy of note that leucine yields a creatine, whilst α-methylamidocaproic and α-ethylamidocaproic acids yield creatinines.

C. H. B.

Alkaloïds. By O. de Coninck (*Compt. rend.*, **104**, 1374—1375).—Nicotine was treated with methyl iodide in the same way as with ethyl iodide (this vol., p. 603). The product is a yellow, translucent solid, which is dissolved in warm, absolute alcohol and gradually mixed with potash of 45°, when a ruby-red coloration is produced, which becomes darker with excess of alkali. If the mixture is heated for 2½ hours on the water-bath, and the alcoholic solution decanted off, and concentrated, at a certain degree of concentration the liquid stains the skin like nitric acid. When evaporated to dryness it leaves a deep reddish-brown, viscid residue, and if this is dissolved in alcohol it gives a solution with a green fluorescence. On addition of water or a concentrated acid this solution becomes turbid, but the addition of hydrochloric acid to the diluted alcoholic solution reproduces the original colour. Ammonia changes the colour to dull red, which is converted by hydrochloric acid into a bright orange-red. If an excess of hydrochloric acid is added to the original alcohol solution, and the mixture poured into a large quantity of water, a brilliant green fluorescence is observed. The liquid is orange by transmitted light, and intense green by reflected light.

These reactions afford further proof that nicotine is closely related to the pyridic or dipyridic compounds. C. H. B.

Separation of the Opium Alkaloïds. By P. C. Plugge (*Arch. Pharm.* [3], **25**, 343—354).—The six alkaloïds narcotine, papaverine, narceïne, thebaïne, codeïne, and morphine are separated by the use of the following precipitants: sodium acetate, potassium ferricyanide, sodium salicylate, potassium thiocyanate, and ammonia. The alkaloïds are obtained as an aqueous solution of the hydrochlorides. The liquid is mixed with a sufficient quantity of concentrated sodium acetate solution, allowed to remain 24 hours, and filtered. The precipitate, washed with a little water, consists of pure narcotine and papaverine; it is dissolved in dilute hydrochloric acid and diluted until the solution contains not more than $\frac{1}{400}$ of narcotine, when a solution of potassium ferricyanide is added. After remaining 24 hours, filtering and washing with a little water, the precipitate of papaverine ferricyanide is obtained from which the alkaloïd may be separated by digesting with aqueous soda, filtering, and if necessary dissolving and reprecipitating with ammonia. The filtrate containing the narcotine yields this alkaloïd by precipitation with ammonia. The filtrate containing the remaining four alkaloïds together with an excess of sodium acetate is concentrated to a small volume on the water-bath and allowed to remain 24 hours, then filtered. The precipitate washed with a little water consists of narceïne separated directly from the liquid as pure alkaloïd. The filtrate contains traces of narceïne and all the thebaïne, codeïne, and morphine. It is mixed with a sufficient quantity of sodium salicylate solution. After 24 hours the crystalline precipitate is filtered and washed with a little water. It consists of thebaïne salicylate. On washing this on the filter with dilute

ammonia until ferric chloride ceases to indicate salicylic acid in the washings, pure alkaloïd remains on the filter. The filtrate contains traces of narceïne, thebaïne, the excess of sodium salicylate, and all the codeïne and morphine. It is acidified with hydrochloric acid; after remaining some time the salicylic acid separated is filtered off, and the filtrate is repeatedly shaken with chloroform to remove the remainder of the salicylic acid, narceïne, and thebaïne; then the chloroform is removed by a gentle heat, the liquid is carefully neutralised and finally mixed with potassium thiocyanate solution. After 24 hours the precipitate consists of codeïne hydrogen thiocyanate. The filtrate contains the morphine, which can be precipitated by slight excess of ammonia. In many cases the above methods can be employed quantitatively. Mixtures of narcotine and morphine precipitated with sodium acetate gave from 97·15 to 100 per cent. of the narcotine. Narcotine in presence of morphine, codeïne, and thebaïne gave 99·43 per cent. Papaverine precipitated by acetate in presence of morphine gave 98·15 per cent. of the total present. The same alkaloïd in presence of morphine, codeïne, and thebaïne gave 97·02 per cent. In the two experiments where thebaïne was present over 90 per cent. of that alkaloïd was obtained by precipitating with sodium salicylate. The separation of papaverine by means of potassium ferricyanide is very complete. Codeïne cannot be quantitatively separated from morphine by means of potassium thiocyanate.

J. T.

Composition of Papaverine. By P. C. Plugge (*Arch. Pharm.* [3], **25**, 421—425).—The composition of this alkaloïd is sometimes represented by the formula $C_{20}H_{21}NO_4$, as given by v. Merck, its discoverer, and sometimes by $C_{21}H_{21}NO_4$. The author shows that the former and older formula most nearly agrees with analytical results obtained both by himself and others. J. T.

Strychnine and Brucine Ferro- and Ferri-cyanides. By Holst and Beckurts (*Arch. Pharm.* [3], **25**, 313—315).—*Normal strychnine ferrocyanide*, $(C_{21}H_{22}N_2O_2)_4,H_4Fe(CN)_6 + 4H_2O$, is precipitated from neutral solutions of strychnine salts by potassium ferrocyanide, forming a white, crystalline powder with a shade of yellow, slightly soluble in cold water, more easily in hot, from which well-formed, prismatic crystals separate on cooling. *Acid strychnine ferrocyanide*, $(C_{21}H_{22}N_2O_2),H_4Fe(CN)_6$, is precipitated from a strong hydrochloric acid solution of a salt by potassium ferrocyanide as a white powder with a shade of blue. It is insoluble in cold water and alcohol, but dissolves in hot water with formation of hydrogen ferrocyanide, giving rise to a blue coloration and the formation of hydrocyanic acid. The salt has a strong acid reaction, decomposes carbonates and is decomposed by ammonia and alkalis with separation of strychnine. *Normal brucine ferrocyanide*, $(C_{23}H_{26}N_2O_4)_4,H_4Fe(CN)_6 + 4H_2O$, is obtained by adding to a concentrated neutral brucine hydrochloride solution, a concentrated solution of potassium ferrocyanide, as tufts of yellow, prismatic crystals; it gives yellow solutions with water and alcohol. In the air it gradually passes into brucine ferricyanide with the separation of brucine. *Acid brucine ferrocyanide*,

$$(C_{23}H_{26}N_2O_4),H_4Fe(CN)_6,$$

the salt precipitated from a very concentrated strongly acid solution of brucine by potassium ferrocyanide, forms a white, crystalline powder, as seen under the microscope, which in the air quickly becomes blue. In less concentrated solutions there is no change at first, but after 12—24 hours beautiful, large, white prisms form of the same composition as the powder. The salt decomposes when heated with water with separation of hydrocyanic acid.

Potassium ferricyanide gives only normal salts. *Strychnine ferricyanide*, $(C_{21}H_{22}N_2O_2)_6,H_6Fe_2(CN)_{12} + 12H_2O$, precipitated from neutral and acid solutions, forms golden-yellow, flat prisms, somewhat sparingly soluble in water to a yellow liquid. *Brucine ferricyanide*, $(C_{22}H_{26}N_2O_4)_6,H_6Fe_2(CN)_{12} + 12H_2O$, is precipitated from acid or neutral solutions of brucine salts as greenish-yellow spangles, sparingly soluble in water to a yellow liquid. Other alkaloïds are now undergoing investigation by the authors.

Estimation of Strychnine and Brucine.—The authors have based a volumetric method on Dunstan and Short's observation that strychnine is completely precipitated from aqueous solution of its sulphate, whilst brucine is not. If a 0·5 to 1 per cent. solution of the two alkaloïds, strongly acidified with hydrochloric acid, is treated with potassium ferrocyanide until a filtered portion of the solution gives a blue stain with ferric chloride paper, the whole of the strychnine is precipitated as acid strychnine ferrocyanide, whilst the brucine remains in solution. The amount of strychnine can thus be determined by using a standard solution of ferrocyanide, 244 parts potassium ferrocyanide corresponding to 334 parts of strychnine. If the solution contain less than 0·5 per cent. the separation is too slow; also the ferric chloride paper should not be allowed to get perfectly dry before use. A mixture containing 0·145 gram strychnine and 0·036 gram brucine gave 0·148 gram of strychnine. To estimate the alkaloïds when occurring together in, say, tinctura strychni, the total weight of the two is ascertained, then, according to Schweissinger, an excess of centinormal hydrochloric acid is added and the excess determined by centinormal soda solution. The neutral solution thus obtained is concentrated sufficiently and titrated with standard potassium ferrocyanide. A mixture containing 0·1 gram strychnine and 0·05 gram brucine gave 0·1017 of the former and 0·04915 of the latter.

J. T.

Sulphonic Acids of Strychnine. By I. Guareschi (*Gazzetta*, **17**, 109—115).—Loebisch and Schoop have recently described a monosulphonic acid of strychnine; the author finds that if strychnine is warmed with three to four times its weight of sulphuric acid, a monosulphonic acid is formed, which is best purified by means of the barium salt. The analyses, though somewhat discordant, point rather to a formula $C_{21}H_{21}(SO_3H)N_2O_2$; it is a yellow, amorphous solid, soluble in acids and alkalis; it does not give the strychnine reaction with potassium dichromate. A solution of its ammonium salt gives precipitates with salts of silver, iron, copper, barium, and lead. Heated at 120—130° it assumes an azure-violet colour. It does not seem to be poisonous.

The disulphonic acid, $C_{21}H_{20}(SO_3H)_2N_2O_2$, was not isolated, but the

barium, sodium, and potassium salts are described as amorphous solids, readily soluble in water, sparingly soluble in alcohol.

V. H. V.

Chelidonine, Chelerythrine, and Sanguinarine. By A. Henschke (*Chem. Centr.*, 1887, 243).—Chelidonine is a tertiary base; analyses of the free base, its salts and the platino- and auro-chloride, point to the formula $C_{20}H_{19}NO_3 + H_2O$.

Chelerythrine and sanguinarine seem not to be identical; the analyses of the latter, its salts and its platinochloride, point rather to the formula $C_{17}H_{15}NO_4$, proposed by Naschold, than to $C_{19}H_{17}NO_4$, that given in most text-books. V. H. V.

The Alkaloïds of Lobelia. By G. Dragendorff and H. v. Rosen (*Chem. Centr.*, 1886, 873). — The authors have isolated from the *Lobelia nicotianæfolia* a second alkaloïd additional to the already known lobeline. It is dissolved by chloroform from solutions made alkaline with ammonia. The alkaloïds exhibit no characteristic colour reactions; they are distinguishable by their behaviour towards the group reagents. In physiological properties they are closely similar.

C. F. C.

Amount of Oxygen taken up in the Decomposition of Hæmoglobin into Albumin and Hæmatin. By M. Lebensbaum (*Monatsh. Chem.*, **8**, 166—179).—The amount of oxygen absorbed in the decomposition of oxyhæmoglobin depends on the time allowed for the experiment, the absorption continuing after 55 days. This is probably due to the albumin which is formed taking up oxygen in presence of alkali (Nencki and Sieber, Abstr., 1882, 1307). Carbonic oxide hæmoglobin behaves in a manner similar to oxyhæmoglobin, but the amount of oxygen absorbed is always less.

Oxyhæmoglobin in 0·1 per cent. sulphuric acid solution, absorbs 1·1 per cent. of its weight of oxygen. N. H. M.

Compound of Hæmatin with Nitric Oxide. By G. Linossier (*Compt. rend.*, **104**, 1296—1298).—An alcoholic solution of hæmatin or reduced hæmatin readily absorbs nitric oxide, forming a brilliant red, non-dichroic solution. The absorption spectrum of this liquid is similar to that of oxhæmoglobin, and consists of two bands between E and F, the breadth of which depends on the concentration of the solution. It is difficult to distinguish this spectrum from that of oxyazotised hæmoglobin, but the latter is somewhat more intense and its two bands are about equal in intensity. When oxyazotised hæmoglobin is mixed with potash, it is converted into oxyazotised hæmatin, which gives an absorption spectrum identical with that obtained by synthesis.

Oxyazotised hæmatin is less soluble in ammoniacal alcohol than ordinary hæmatin, and reducing agents have no action on this solution. The oxygen of the air converts it into hæmatin and ammonium nitrite. If the solution thus converted into hæmatin by the action of oxygen is treated with a reducing agent, it first forms reduced hæmatin and then oxyazotised hæmatin. The reducing agent acts on the hæmatin and also on the ammonium nitrite, converting the former

into reduced hæmatin, liberating nitric oxide from the latter. The reduced hæmatin and nitric oxide at once combine to form oxy-azotised hæmatin, which is not further affected by the reducing agent.

The author points out that hæmatin should by analogy be called oxyhæmatin, whilst the name hæmatin strictly belongs to the compound commonly known as reduced hæmatin (Hoppe-Seyler's hæmochromogen). He proposes to change the names in this way, in order that oxyhæmatin and hæmatin may correspond respectively with oxyhæmoglobin and hæmoglobin. C. H. B.

Melanin. By M. Miura (*Chem. Centr.*, 1887, 250).—To prepare melanin, an emulsion of a melanotic spleen is diluted with water and treated with calcium chloride and sodium phosphate. The precipitate formed contains the colouring matter, and after frequent washings at 40° is treated with a powerful digestive fluid until the solution ceases to give the peptone reaction. The residue is treated with soda, and washed to remove the nuclein and fatty acids, and finally treated with alcohol and ether. The melanin forms a brownish-black powder, possessing the properties and composition of the hippomelanin of Berdez and Nencki. Experiments showed that the urine of animals into which melanin had been injected, gave the melanogen reaction. As the injection of melanin produces no increase in the indican reaction of the urine, it is probable that the dye formed in the air or on oxidation is analogous to the dye obtained by Pribram from the urine of a patient suffering from a melanotic tumour, which is allied to or identical with the melanin of Dressler. V. H. V.

Physiological Chemistry.

Action of Oxygen on Animals. By B. W. Richardson (*Chem. News*, **55**, 253).—According to experiments described in this paper, whilst an atmosphere of pure, freshly-made oxygen gas constantly renewed has no narcotic effect on animals, the result is quite otherwise if the oxygen that has passed through the chambers containing the animals be used a second time, and this even when the gas has been dried, and freed from carbonic acid, ammonia, and all appreciable impurities before being returned. In this case the animals become drowsy, and, as the experiment proceeds, the drowsiness passes into a perfectly quiet sleep, which ends in death after several repetitions of the process, although by no chemical tests can any difference be discovered between the lethal and the freshly-prepared oxygen. But the gas that has thus become "devitalised" can readily be "revitalised" by electrical brush discharges from the positive pole of a frictional machine. The lethal oxygen supports combustion as vigorously as ordinary oxygen, and supports life in cold-blooded animals.

R. R.

Composition of Blood, Liver, and Flesh under varying Conditions. By H. Weiske and others (*Bied. Centr.*, 1887, 315—

318).—The action of acidified food on the composition of portions of a lamb was examined. Three lambs of like age were chosen, of which one (3) was immediately killed and analysed, whilst the other two were permitted to live for another six months; but whilst one (1) received ordinary hay, the hay which was given to the other (2) was moistened with dilute sulphuric acid. Analyses of the bones, &c., of these lambs after death showed that the bones of lamb (1) contained 2 per cent. more mineral matter than those of (2), and that this 2 per cent. consisted principally of lime and phosphoric acid. The dry matter of the blood of all three showed no appreciable difference, and the same may be said for the liver, but in the flesh, although nearly all constituents are present in like quantities, the lime in (1) was double in quantity. E. W. P.

Animal Nutrition. By J. W. Sanborn (*Bied. Centr.*, 1887, 383—386).—Two sets of steers were fed with Timothy hay and with straw, hay, and meal. The result was that an almost like increase in live-weight took place; it was further found that as the time proceeded so was a larger amount of food necessary to produce 1 lb. increase in weight of the skeleton of the animal, although at the same time the nutrient ratio varied considerably, also the increase in fat seemed to be the same. Ensilage seemed to affect the quantity of cream in milk. E. W. P.

Variations in the Proportion of Phosphoric Acid in Milk. By A. Andouard (*Compt. rend.*, **104**, 1298—1300).—The proportion of phosphoric acid in milk diminishes from the beginning to the end of lactation, the degree of reduction varying with different animals. The amount of fat, and especially of sugar, diminishes at the same time. Out of four cows, two showed an increase in the proportion of caseïn, and two a decrease. The increase in the total solid matter during lactation is not a constant quantity. The age of the cows affects only the quantity of milk given, the youngest giving the least. Contrary to the statement of Kroemer, green fodder gives better results than dry fodder. The best of the foods used in the west are cabbages and legumes; next in order of merit come potatoes, swedes, beetroots, and maize. The abundance and composition of the milk appears, however, to depend mainly on the individuality of the animal. C. H. B.

Excretion of Urea and Uric Acid from the Human System. By Mares (*Chem. Centr.*, 1887, 339—340).—The author has conducted a series of experiments on the effect produced by starvation on the proportion of urea and uric acid excreted from the human system. As a result from 21 persons it follows that in a state of starvation, a constant quantity of uric acid is excreted within a given time without reference to the quantity of nitrogen excreted within the same period. The quantity of uric acid is conditioned by the age of the individual, being diminished with greater age, but it is not influenced by the greater or less quantity of meat taken by the individual before starvation. The quantity of nitrogen, however, does

not depend on this latter condition, and varies as much as 120 per cent. within the same interval of time, increasing at the sixth to ninth hour after a meat meal, and reaching its maximum at the 24th hour. The explanation given of the results is as follows:—The uric acid is a product of living protoplasm, whilst the urea is derived from absorbed albuminoïds. In a state of rest, the protoplasm produces the uric acid, whilst the quantity of urea changes according to the greater or less quantity of albuminoïds absorbed. With an albuminoïd diet, the protoplasmic cells of the digestive tract are called into instant action, whilst the protoplasm is decomposed for the production of the digestive fluids; the quantity of uric acid is accordingly increased. So soon as the cells are at rest, the production of uric acid decreases, the resorption of the albuminoïds begins, and concomitantly the formation of urea. Experiments are given in proof of this point. If then uric acid is considered as a product of decomposition of protoplasm, the quantity of the acid eliminated may be taken as a measure of the amount of the decomposition.

V. H. V.

Hydroxybutyric Acid in Diabetic Urine. By Wolpe (*Chem. Centr.*, 1887, 277—278).—The author has examined the urine of 10 diabetic patients for ammonia, hydroxybutyric acid, and acetone. The results show that the proportions of ammonia and hydroxybutyric acid do not vary concomitantly. After a dose of sodium carbonate, the proportion of ammonia is diminished or even disappears, but hydrochloric acid produces sometimes no effect and sometimes an increase, whilst the proportion of hydroxybutyric acid is not thereby diminished. A flesh diet produces an increase of both constituents. Apparently there is no fixed relation between the quantities of acetone and hydroxybutyric acid eliminated; however, the proportion of acetoacetic acid, as shown by the ferric chloride test, and of hydroxybutyric acid, vary in a parallel degree. There is also no relation between the quantity of sugar and the other pathological products. In a case of coma diabeticum, a gas analysis of blood from the veins gave 19·5 instead of 35 volumes per cent. of carbonic anhydride.

V. H. V.

Physiological Action of Chlorinated Ethyl Sulphides. By V. Meyer (*Ber.*, **20**, 1729—1731).—Dichlorethyl sulphide, $S(C_2H_4Cl)_2$, causes intense inflammation and suppuration when in contact with the skin or when breathed. The monochloro-derivative $SEt{\cdot}C_2H_4Cl$, shows similar but feebler action, whilst ethyl sulphide is without action. From this it follows that in these substances the physiological action is entirely and directly dependent on the chlorine. A. J. G.

Physiological Action of Tertiary Alcohols on the Animal Organism. By B. M. Shapiroff (*Vrach*, **19**, 1887, 388—389).—Dimethyl ethyl carbinol, when introduced under the skin of a frog, in quantities of from 0·001 to 0·005 gram, produces first stupor (depression of the cerebral hemispheres) and then paralysis of the spinal cord, as shown by the arrest of the lymphatic heart, the centres for which reside in the cord. No direct effect is produced on the blood circulation. In dogs and rabbits the blood pressure is diminished,

the vasomotor centres being paralysed. No direct effect is produced on the heart. The temperature is reduced considerably. Trimethyl carbinol acts in the same way, but less powerfully. The author deduces from his experiments that whilst primary alcohols have a generally stimulating action, tertiary alcohols, even though isomeric with them, act as depressants. T. M.

Myoctonine. By G. Dragendorff and S. Salomonowitsch (*Chem. Centr.*, 1886, 861).—This alkaloïd occurs, together with lycaconitine (*Chem. Centr.*, 1884, 29) in *Aconitus lycoctonum;* it differs from the latter in melting point (144°) and solubilities. It is freely soluble in chloroform, nearly insoluble in ether. Lycaconitine being on the other hand soluble in ether, the separation of the alkaloïds is effected by means of this menstruum. The physiological action of the alkaloïds is closely similar. The lethal dose of the myoctonine, in the case of frogs, is 0·01 gram; characteristic symptoms of its action are obtainable with 0·00003 gram. These are, in the main, paralysis of the extremities of the motor nerves, the medulla and nerve trunks remaining unaffected, as also the muscular irritability. The injection of 0·025 gram of the nitrate into the vena jugulari of cats caused instantaneous death; the subcutaneous injection of 0·1 gram caused death within 20 to 30 minutes. Twice this quantity introduced per os caused similar results.

For the isolation of myoctonine from animal fluids, the authors recommend shaking with benzene, after the usual preliminary purification, and rendering alkaline with ammonia. After death caused by subcutaneous injection, the alkaloïd is found in the coats, but not the contents, of the stomach and intestines; in the blood, liver, and kidneys in relatively large quantity; in small quantity in the pancreas. C. F. C.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification. By A. Celli and F. Marino-Zuco (*Gazzetta*, **17**, 99—103).—In the course of analyses of water from the subsoil of Rome, amongst other organisms a micrococcus of globular form (*Micrococcus cereus*) was discovered; this was found to be a very efficacious nitrifying agent.

Preliminary experiments are quoted to prove that for the process of nitrification the presence of bacteria is not absolutely essential, for if sterilised solutions of ammonium salt are filtered through sterilised sand or platinum sponge, nitrification ensues to an appreciable degree. It is further shown that among the organisms which liquefy nutritive gelatin *Bacillus saprogenus*, *B. fluidificans*, and *Micrococcus luteus*, when thrown on to sand in cultivating liquids, not only do not produce nitrates but destroy them completely; on the other hand these same

organisms, taken from potato-cultures, far from destroying the nitrates, are among the most active agents in producing them.

V. H. V.

Action of Alkaloïds in the Animal and Vegetable Kingdom. By A. Marcacci (*Chem. Centr.*, 1887, 248).—Fermentation of milk was promoted by addition of water, potassium and sodium sulphate, sodium chloride, atropine and morphine sulphate, but impeded by veratrine sulphate, quinine hydrochloride, cinchonamine sulphate, and especially by strychnine sulphate. Solutions of the above salts, with the exception of those of cinchonamine and quinine, as compared with the water, promote alcoholic fermentation. In order to study the action of alkaloïds on seeds, the latter were either soaked in the solutions and then planted out, or allowed to sprout and grow in powdered glass, and then watered with the solution. The sprouting process was hardly influenced by salts of morphine, but affected by those of strychnine, veratrine, and especially of quinine and cinchonamine. The alkaloïd salts have a most injurious effect on maize, beans, and lupines. On already developed plants, morphine salts produce no effect, but salts of strychnine, and especially quinine and cinchonamine, are very detrimental. Strychnine hinders the development of frog spawn, but morphine and atropine favour it as compared with distilled water. Tadpoles are quickly killed in solutions of salts of veratrine, strychnine, and quinine, but more slowly in atropine and distilled water; whilst frogs are more quickly killed by strychnine and veratrine, but will live for several months in a solution of morphine. As regards the effect of poison, there appears to be no marked difference between animal and plant protoplasm, nor a definite classification into animal and plant poisons. V. H. V.

Are Nitrates formed in the Organism of Higher Plants? By E. Schulze (*Ber.*, **20**, 1500—1504).—Lupin sprouts grown on paraffined gauze stretched over flat vessels filled with distilled water, were found to be free from nitrates. On the other hand, when the lupin sprouts were grown in a moist sand, they were found to contain nitrates. It is shown that nitrogenous substance is taken up by the water, and that this is partially converted into nitrates in presence of sand. The author does not insist that the nitrates found in the sprouts grown in sand can only have been formed from nitrogenous substance separated from the roots, but maintains that the presence of nitrates is no proof of Berthelot and André's view, that nitrates are formed in the organism of higher plants (compare also this vol., p. 686). N. H. M.

Carrotene in Leaves. By A. Arnaud (*Compt. rend.*, **104**, 1293—1296).—Carrotene (Abstr., 1886, 711) is always found in the leaves of plants in full vegetation.

Leaves dried in a dry vacuum contain the whole of the original carrotene, but this is not the case if they are dried by heat. Light petroleum boiling below 100°, and free from benzene, dissolves carrotene, but not chlorophyll. Carrotene dissolves in almost any

proportion in carbon bisulphide, forming a solution with an intense blood-red colour.

A known weight (20 grams) of the leaves dried in a vacuum, is treated with a definite volume (1000 c.c.) of light petroleum boiling below 100°, and is allowed to remain at the ordinary temperature for 10 days, with occasional shaking. A definite fraction (100 c.c.) is placed in a dish, allowed to evaporate to dryness, and the residue dissolved in carbon bisulphide so that the solution measures 100 c.c., which will correspond with one-tenth of the total carrotene present in the weight of leaves taken. The intensity of the colour of the solution is measured by means of a Duboscq colorimeter, and is compared with a solution of pure carrotene of known strength.

The amount of carrotene is equal on an average to about 0·1 per cent. of the weight of the dried leaves, and it must exert a considerable influence on the colour of the leaves. C. H. B.

Organic and Inorganic Constituents of Grapes. By E. List (*Chem. Centr.*, 1887, 245—246).—The author has made an investigation into the organic and inorganic constituents of grapes of the Franconia district, as influenced by the nature of the soil and the manure applied, and examined the action of various ferments on the pressed juice. Results are given of (i) the composition of 39 various species; (ii) the proportion of mineral matter present in the juice; (iii) the percentage composition of the ash; and (iv) the composition of the fermented juice. From the results it follows (i) that the proportion of each constituent varies within wider limits than hitherto supposed; (ii) the ratio 100 : 7 of alcohol to glycerol as a minimum is not absolute; and (iii) the ferments abstract from the juice a considerable quantity of phosphates, but these are again returned after some time to the wine on the breaking down of the ferment-cells.

V. H. V.

Solanine. By G. Kassner (*Arch. Pharm.* [3], **25**, 402—403).—Siftings from diseased potatoes gave as much as 0·03—0·05 gram of solanine from 120 grams, whilst sound potatoes of the same kind gave scarcely any. The observations were made in January, showing that solanine may be formed in potatoes during the period of winter rest.

J. T.

Tunisian Soils. By H. Quantin (*Compt. rend.*, **104**, 1528—1529).—A series of determinations of nitrogen and phosphoric acid in soils in various parts of Tunis. In the valley of the Medjerdah the soils show a deficiency in phosphoric acid, a result which is due to the growth of cereals from time immemorial without any restitution of phosphates being made. This is the cause of the mediocre crops which are now obtained, and the deposits of phosphates recently found by Thomas in Tunis will be of very great value as a means of restoring fertility to the exhausted soils. C. H. B.

Evolution of Ammonia from Vegetable Soils. By Berthelot and André (*Compt. rend.*, **104**, 1219—1224).—The soil, which had undergone no previous treatment, was placed in a flask and subjected to a current of air, which was afterwards passed through cotton-wool

and then through bulbs containing dilute standard sulphuric acid. In other cases the soil was placed under a bell-jar, together with a dish containing the acid.

Vegetable soils evolve ammonia spontaneously, in consequence of the slow decomposition of the ammoniacal and amidated compounds present in the soil. This decomposition is partly due to the chemical action of the water, carbonates, &c., and partly to physiological actions such as fermentation, the development and activity of microbes, and vegetation proper. Most of the reactions concerned in the evolution of the ammonia are non-reversible.

A comparison between the amount of ammonia evolved from the soil, and the amount present in the atmosphere, and therefore capable of being absorbed by the soil, was made by supporting a flat dish containing sulphuric acid just above the top of the grass in a grass-field, the dish being protected at night and during rain and the loss by evaporation being compensated by addition of water. A similar dish was supported inside an earthenware cylinder which isolated a portion of the soil and grass from the surrounding soil. Care was taken that the duration of the experiment was not sufficiently long for the grass enclosed in the cylinder to become etiolated. The sulphuric acid was not titrated, but was made alkaline and distilled.

The amount of ammonia existing in the air is extremely variable, and changes with every change in meteorological conditions. The evolution of ammonia from the soil is much more regular; it is in fact conditioned by comparatively regular natural processes. In all cases there is no necessary connection between the tension of the ammonia in the atmosphere and the evolution of this gas from the soil. The two phenomena, the absorption of ammonia by the soil from the air and the evolution of ammonia from the soil into the air, are independent of one another. C. H. B.

Agricultural Value of Retrograde Phosphate. By J. Joffre (*Bull. Soc. Chim.*, **47**, 312—316).—The coefficient of solubility of ferric phosphate, known as retrograde phosphate, in water is about 0·000002, and therefore differs but little from that of raw, or tricalcium phosphate. Experiments conducted on crops show that the use of tricalcium phosphate has a slight advantage over the retrograde phosphate. The following results were obtained, 22·5 kilos. of combined phosphoric acid being applied per hectare in the form of the different manures:—

Without any phosphatic manure	= 1·441	kilos. of grain	per hectare.
With retrograde phosphate	= 1·559	,,	,,
With insoluble phosphatic nodules	= 1·580	,,	,,
With soluble phosphate	= 1·736	,,	,,

A. P.

Analytical Chemistry.

Estimation of Hydrogen Peroxide. By H. Thomas (*Chem. Centr.*, 1887, 283).—The amount of hydrogen peroxide in a solution is estimated by acidifying with sulphuric acid, adding a solution of potassium iodide free from iodate, and determining the iodine liberated by means of a standard solution of sodium thiosulphate.

V. H. V.

Volumetric Estimation of Iodine. By T. Salzer (*Chem. Zeit.*, **11**, 754).—The degree of dilution of the sodium sulphite solution used in estimating iodine by Kalmann's process materially influences the result. With a constant degree of dilution, however, the author states that the results agree very well amongst themselves.

J. P. L.

Determination of Sulphuric Acid in Water. By Fricke (*Chem. Centr.*, 1887, 283).—As various methods suggested for the determination of sulphuric acid in samples of water are far from accurate, the following process is proposed; 200 c.c. of the water is boiled with a few drops of a solution of sodium carbonate to precipitate the lime. The volume is again made up and 100 c.c. withdrawn by a pipette, neutralised, and boiled with baryta-water of known concentration; the excess of the baryta is precipitated by carbonic anhydride, and the whole boiled. The precipitate of sulphate and carbonate is filtered off, and the latter decomposed by a decinormal solution of hydrochloric acid. From the quantity of the solution used the excess of the barium hydrate is calculated, and deducting this, the amount of the hydrate required to precipitate the sulphuric acid is calculated. The formation of a soluble acid barium carbonate not decomposed by boiling on passing in the carbonic anhydride, is a source of error too small to be appreciable. V. H. V.

Estimation of Nitrogen in Organic Substances. By Raulin (*Bull. Soc. Chim.*, **47**, 94—97).—A modification of Dumas' process. The tube in which the combustion is conducted is of copper, about 3 mm. thick, and having an internal diameter of 18 mm. The length of the tube is 1800 mm., and arranged along it at equal distances are four small brass water-jackets, each about 100 mm. in length, one of which is placed at either end, and the other two at equal distances between, thus dividing the outside surface of the copper tube into three portions of about 500 mm. each. In each of these uncovered portions of the tube a separate combustion is conducted; the space nearest the front is first charged by introducing a coil of sheet copper about 60 mm. long; with the aid of a glass funnel 60 grams of small fragments of copper oxide are then added, and finally a convenient weight of the organic compound mixed with a small quantity of fine copper oxide and about 20 grams of coarser fragments; the funnel and back part of the tube are then rinsed down with a small quantity of copper oxide, and a second and third charge

successively introduced in a similar manner into the two remaining portions of the tube between the cooling jackets. The whole tube is supported at the four points at which the water-jackets are fixed, and the combustion is effected by a small movable furnace. The back part of the tube is connected with a continuous supply of pure carbonic anhydride, and the front end is fitted with a delivery tube passing into a solution of potassium hydroxide, in which graduated glass collecting tubes are arranged. After driving out all the air from the tube, the combustions are conducted in turn, that at the front of the tube being first performed. A deduction is made in each experiment for gases not absorbable by potash introduced with the carbonic anhydride, which amount varies with the duration of the experiment, and is carefully determined previously by blank experiments. A. P.

Kjeldahl's Method for Estimation of Nitrogen. By K. Ulsch (*Chem. Centr.*, 1887, 284).—In a former paper the author has recommended the use of platinic chloride to accelerate the oxidation of organic substances by boiling sulphuric acid; it is here noted that an excess must be avoided as hindering rather than promoting the reaction. If platinum chloride is used, concentrated acid is required, and the solution or extract to be examined must be evaporated; the heating must not be prolonged after the reaction is completed, otherwise a loss of nitrogen occurs; three to four minutes is sufficient. As regards Wilfahrt's modification, it is remarked that before the distillation of ammonia, after saturation with alkali, potassium sulphide must be added. The same result is produced by using a saturated solution of ferrous oxide. V. H. V.

Estimation of Nitrogen in Urine. By L. Garnier (*J. Pharm.* [5], **15**, 557—559).—Pflüger and Bohland (Abstr., 1885, 608) have given a method based on the decomposition of the urine when heated with a mixture of concentrated and Nordhausen sulphuric acids. The nitrogenous compounds are transformed into ammonia, which is fixed by the excess of acid. The ammonia is displaced by heating with soda solution, and is collected in standard sulphuric acid. The author has frequently used the method, but as Nordhausen acid often contains ammonia, he employs instead a mixture of one part of pure sulphuric anhydride and three parts of concentrated sulphuric acid. Numerical results given show that the method is very satisfactory. J. T.

Organic Nitrogen in Chemical Manures. By Gassaud (*Compt. rend.*, **104**, 1632—1633).—It is frequently important to ascertain the origin of the organic nitrogen in artificial manures. In a case which came under the author's notice, the behaviour of the manure on heating indicated the presence of hides, or, in other words, the presence of the residues from tanneries. The manure was therefore extracted with water and the solution treated with ferric chloride, potassium dichromate, ferric acetate, and magenta, with which it gave blue, brown, deep bluish-violet, and red precipitates respectively. Similar or identical reactions were obtained with infusions of hides

and of tannin, whilst infusions of horns, flesh, blood, &c., gave no similar results. C. H. B.

Estimation of Phosphoric Acid. By C. Mohr (*Chem. Zeit.*, **11**, 417—418).—Solution of the phosphatic substance is effected by means of dilute sulphuric acid. For this purpose, 2 grams of the substance is treated with successive small quantities of 2 per cent. sulphuric acid in a mortar. The residue is added to the extracts and the whole made up to 100 c.c. exactly and allowed to digest for one hour. 10 c.c. of the filtered solution corresponding to 0·2 gram are then treated with potassium ferrocyanide so long as iron is precipitated. After the addition of sodium acetate, the phosphoric acid is titrated in the usual way with a standard solution of uranium acetate. It is stated that the end reaction is not influenced either by an excess of potassium ferrocyanide or by the presence of the Prussian blue. J. P. L.

Detection of Boron in Milk and other similar Fluids. By M. Kretzschmar (*Chem. Zeit.*, **11**, 476—477).—5 to 6 c.c. of the sample to be tested is placed in a platinum crucible and gently evaporated to one-third; after the addition of 5 or 6 drops of fuming hydrochloric acid, the residue is again evaporated and a Bunsen burner held over the mouth of the crucible. The presence of boron is easily detected by the intense green colour imparted to the flame. J. P. L.

Estimation of Potassium in Ashes and Minerals. By M. Kretzschmar (*Zeit. Chem.*, **11**, 418).—In cases where the estimation of potassium only is required, the following process will be of use.

5 grams or more of the substance is dissolved in a flask with hydrochloric acid if possible, a drop of nitric acid being added to oxidise any ferrous iron. The solution is boiled and the sulphuric acid precipitated with barium chloride; whilst still hot the solution is treated with ammonia and ammonium carbonate in excess. Instead of filtering and washing this cumbersome precipitate, the whole is transferred to a porcelain capsule and evaporated to dryness on the water-bath, the residue being finally heated at 110°. The precipitate which is now of small bulk can be easily exhausted with water and a few drops of ammonia.

The washings are made up to 500 c.c. and 50 or 100 c.c. taken for analysis. If magnesia is present in any considerable quantity, oxalic acid must be added to the liquid before evaporation and ignition; if only small quantities are present this may be omitted.

The determination of potash is made in the usual way after removal of the ammoniacal salts by ignition. J. P. L.

Estimation of Lithium and Sodium in Mixtures of their Carbonates. By E. Holdermann (*Arch. Pharm.* [3], **25**, 305—307).—Lithium carbonate when heated to fusion suffers a loss in weight amounting to about 2·15 per cent., but when heated with four times its weight of sodium carbonate no carbonic anhydride is evolved from

the lithium salt. The mixed salts are heated to faint redness until the weight becomes constant. Excess of normal hydrochloric is added, the mixture heated on the water-bath to expel carbonic anhydride, and the excess is titrated with normal potash solution, using phenolphthaleïn as indicator. Then by known methods of calculation the respective amounts of lithium and sodium can be ascertained.

J. T.

Calcimetry. By A. Bernard (*Compt. rend.*, **104**, 1525—1528).—A modification of Scheibler's apparatus for the determination of carbonic anhydride in soils, &c.

Determination of Lime and Magnesia in presence of Manganese. By F. Stolba (*Chem. Centr.*, 1887, 285).—To the solution to be examined, ammonia and ammonium chloride are added to slight alkaline reaction, and the liquid heated to boiling; to remove the manganese, potassium permanganate is added until a slight tint is produced; the manganese is precipitated as a peroxide, and the slight excess of the permanganate removed by protracted boiling. The lime and magnesia are determined in the filtrate. This method is also applicable in presence of iron. V. H. V.

Titration of Zinc Powder. By Kupferschlaeger (*Bull. Soc. Chim.*, **47**, 312).—When samples of zinc powder are examined by Weil's method any cadmium or iron present will be calculated as metallic zinc, the author therefore proposes to dissolve the zinc powder in well-boiled dilute sulphuric acid, add ammonium carbonate, filter, and titrate the zinc in the clear solution with standard sodium sulphide.

A. P.

Volumetric Estimation of Alumina. By R. Gatenby (*Chem. News*, **55**, 289).—Alumina, having an alkaline reaction with methyl-orange and an acid one with litmus, can be easily determined when dissolved in aqueous soda, by first determining the amount of the latter by normal acid, using phenolphthaleïn as indicator. A few drops of methyl-orange solution are added to the decolorised liquid, and then the normal acid required to obtain a pink colour gives the amount of alumina and alkaline soda salts together. Litmus solution is then added, and the liquid titrated back with normal caustic soda until a decided blue colour appears. R. R.

Note.—This is essentially K. J. Bayer's well-known method (Abstr., 1886, 281, 651, see also "E. B." *ibid.*, 651) to which, however, no reference is made in the original. A. J. G.

Rapid Estimation of Phosphorus in Iron. By Wedding (*Chem. Centr.*, 1887, 260).—The iron is dissolved in nitric acid, and to it is added a concentrated solution of ammonium molybdate; the precipitate which separates is transferred into a narrow, calibrated tube, and its amount estimated by the volume which it occupies. This method is an improvement on that proposed originally by Eggertz; sufficiently accurate results can be obtained in half an hour,

but it cannot be applied to samples containing more than 0·12 per cent. of carbon. V. H. V.

Determination of Combined Carbon in Iron. By C. Brand (*Chem. Centr.*, 1887, 345).—The well-known method of the direct separation of carbon from iron gives too low results; the method here proposed is applicable only for samples of iron rich in carbon. One gram of the sample is dissolved in 30 to 40 c.c. of hydrochloric acid containing 24 per cent. of bromine; the latter is removed in the form of hydrobromic acid by heating with 3 to 4 grams of ammonium oxalate. The removal is completed after one to two hours; the carbon is collected on an asbestos filter, and in the combustion, the small quantity of bromine absorbed by the carbon is retained by interposing in the combustion-tube a small spiral of silver kept at a red heat. V. H. V.

Separation of Phosphoric Acid from Tungstic Acid. By F. Kehrmann (*Ber.*, **20**, 1811—1814).—All orthophosphotungstates are decomposed into basic tungstates and tribasic phosphates by boiling for half an hour with a sufficiency of aqueous soda. After cooling, the solution is mixed with as much ammonium chloride as would suffice to convert all the alkali present into chloride. Magnesia mixture will now precipitate the phosphoric acid perfectly free from tungstic acid. A. J. G.

New Chloroform Reaction. By A. Jolles (*Chem. Zeit.*, **11**, 786).—If potassium manganate is added to chloroform containing alcohol, aldehyde, or other oxidisable substances, it is reduced to potassium manganite. The rate of this reduction furnishes a rough index to the amount of alcohol or other oxidisable substances in the chloroform. J. P. L.

Chloral Hydrate. By G. Dragendorff and H. Tiesenhausen (*Chem. Centr.*, 1886, 636).—The authors' experiments show that this substance, when present, may be isolated from urine and the contents of the alimentary organs, by exhaustion with ether, after previous purification by treatment with alcohol and filtration. From 100 c.c. of these fluids containing 5 mgrms. of chloral, sufficient was isolated in this way for identification. The method is inapplicable to fluids containing blood, in which case the distillation test is to be recommended.

The isonitrile test for chloral hydrate: warming the isolated and dry substance with alcoholic sodium hydrate and a trace of pure aniline, is extremely sensitive, the product in question being obtained in perceptible quantity from $\frac{1}{64000}$ gram. The naphthol test: blue coloration on warming (50°) with concentrated aqueous potash and a trace of phenol, is also very sensitive, being well marked with $\frac{1}{24000}$ gram of substance. The limit of the formic acid test is reached with $\frac{1}{9000}$ gram of substance; of the lime water and hydrogen sulphide test (pink coloration) with $\frac{1}{1500}$ gram.

The authors find that these reactions are unaffected by the pre-

sence of urochloralic acid, into which a portion of the chloral is usually converted in its passage through the body. C. F. C.

Isolation and Detection of Phenol. By G. Dragendorff and W. Jacobson (*Chem. Centr.*, 1886, 828).—The authors have investigated, with satisfactory results, the application for this purpose of the method employed by them for the isolation of alkaloïds from animal fluids, namely, a preliminary treatment with alcohol after acidification, filtration, evaporation of the alcohol, and shaking with benzene. From liquids containing 1 mgrm. in 100 c.c., sufficient was isolated for identification. For this the authors recommend the Baumann and Jacquemin reactions. Landolt's reaction (bromine) is useful in distinguishing phenol from thymol, the latter yielding an amorphous bromide.

In certain cases, phenol, in its passage through the body, enters into combinations, which cannot be isolated by direct treatment with solvents. These compounds, however, are resolved by warming with acids, which is therefore a necessary preliminary to the isolation of the phenol. C. F. C.

Estimation of Starch and Sugars. By J. Effront (*Bull. Soc. Chim.*, **47**, 5—14).—When a solution containing invert sugar, glucose, maltose, and dextrin is heated at 100° with ammonium hydroxide, the sugars are almost completely destroyed; if now the ammonia is boiled off and the residue treated with sodium hypochlorite the whole of the sugars are removed whilst the dextrin in solution is not affected, and retains its rotatory power unaltered. Further, in opposition to Brown and Heron, the author states that the series of dextrins formed when starch-paste is acted on by diastase have one and all the same rotatory power, and on these results the following method for the estimation of starch is based. Ten parts of the starch are made into a paste, cooled to 50°, and the extract from one part by weight of malt added, the solution is then made up to such a strength that every litre contains 100 grams of starch. As soon as this is broken up into maltose and dextrin, a portion of the solution is diluted so that it may contain from 4 to 9 per cent. of sugar, and the rotatory power is observed; 10 c.c. of the solution is then mixed with 10 c.c. of ammonium hydroxide solution (22° Baumé) and 5 c.c. of water, the mixture is digested at 100° for 40 minutes in a corked flask, concentrated to from 5 to 8 c.c., cooled, 10 c.c. of a solution of sodium hypochlorite containing 7 to 8 per cent. of active chlorine is added, the mixture well shaken, and 2 c.c. of concentrated hydrochloric acid run in. The whole is then made up with water to exactly 25 c.c., and the rotatory power of the liquid thus obtained is observed; the alteration of rotatory power between the first and last observation (account being taken of the difference of dilution) is due to the destruction of the maltose, whilst the final rotatory power indicates the amount of dextrin present, and from these data the amount of starch is calculated.

For the rapid determination of starch in crude farinaceous substances such as grain, potatoes, &c., the author advises the use of a

modification of Dubrunfauts' method. Three grams of the starchy material are ground up in a mortar with 20 c.c. of concentrated hydrochloric acid and left for 30 minutes; the solution is then poured into cold water and made up to 200 c.c., filtered, and the rotatory power due to the dissolved starch observed; from this the amount of starch actually present is calculated. Thus conducted this method gives results which may be as much from 2 to 3 per cent. in error. If it is desired to make an accurate determination of the starch in raw products, the author converts the starch into dextrin and maltose according to the directions given by Mercker in his *Handbuch der Spiritusfabrikation*, 2nd edition, he then destroys the maltose by means of ammonia and sodium hypochlorite, and proceeds as in the first of the two foregoing methods. A. P.

Estimation of Starch. By A. v. Asboth (*Chem. Zeit.*, **11**, 785—786).—This process depends on the fact that barium hydroxide forms an insoluble compound of definite composition with starch.

The estimation is performed in the following manner:—3 grams of finely-ground substance is repeatedly treated with small quantities of water in a porcelain mortar. The washings and residue, which should measure about 100 c.c., are transferred to a 250 c.c. flask. The flask is then heated on a water-bath and frequently shaken during the conversion of the starch into paste. To the starch solution, when cool, 50 c.c. of standard baryta-water is added, and then alcohol to 250 c.c. After the precipitate has settled, the excess of barium hydroxide is determined in 50 c.c. of the clear liquid. The formula for the barium compound is $(C_6H_{10}O_5)_4BaO$. Dextrin if present would also be precipitated, and therefore count as starch. A full description of the process, with the results of several test analyses, is given in the *Analyst* for July, 1887. J. P. L.

Estimation of Starch in Potatoes. By A. Girard (*Compt. rend.*, **104**, 1629—1632).—Pure potato starch gelatinised by heat or by the action of dilute potash or cuprammonium solution, and then acidified with acetic acid and titrated with dilute iodine solution, absorbs a quantity of iodine which is practically constant, and is equal to 0·122 gram per gram of anhydrous starch.

In order to estimate the amount of starch in potatoes, 25 grams of a grated sample is placed in a flask of 750 c.c. capacity, mixed with 50 c.c. of 0·2 per cent. hydrochloric acid, and allowed to remain 2 to 3 hours, 100 c.c. of a solution of cupric oxide in ammonia is added to the acid liquid and the mixture allowed to remain over-night. It is then acidified with acetic acid and titrated with a solution prepared by dissolving 3·05 grams of pure iodine and 4 grams of potassium iodide in 1000 c.c. of water, starch-paper being used as an indicator. 10 c.c. of this normal solution = 0·25 gram of starch, and a decinormal solution is prepared from it. In actual work an approximate estimation is first made with the normal solution, and a second titration is afterwards made, the decinormal solution being used towards the end of the reaction.

A correction is necessary in consequence of the dilution of the

liquid and the absorption of iodine by proteïd substances in the potatoes. This may be taken as equivalent to 0·5 part of starch per 100 parts of potatoes. C. H. B.

Estimation of Acetic Acid in Acetates by Direct Titration. By A. Sonnenschein (*Chem. Zeit.*, **11**, 591—592).—The author has devised a rapid and accurate process for the determination of acetic acid in acetates. The process is based on the fact that whereas methylaniline-orange (Orange No. 4) is unaffected by acetic acid it is changed to a red by mineral acids.

The carbonate, which is always present in commercial acetates, can be determined by titration in the same solution employed for the titration of the acetic acid, provided the amount of colouring matter is small. A solution of the acetate is prepared containing 5 grams of acetate in 250 c.c. of water, and 50 c.c. of this solution is taken for analysis. The carbonate is titrated by means of normal hydrochloric acid, using phenacetoline as an indicator. The red colour changes to yellow with an excess of hydrochloric acid. From the hydrochloric acid used the carbonate can easily be calculated. A few drops of methylaniline-orange are now added to the solution and the titration with normal hydrochloric acid continued. So long as acetic acid is present no change of colour takes place, but with an excess of hydrochloric acid, the red colour appears. The amount of acetic acid can readily be calculated from the amount of normal hydrochloric acid used. If the amount of colouring matter masks the phenacetoline reaction, the carbonate can be determined by precipitation with barium chloride. In the case of commercial acetate of lime, the solution is as a rule so strongly coloured that it is necessary to remove the colouring matter before titration. To decolorise the solution the author employs about 3 grams of tutty, and at the same time passes a stream of carbonic anhydride through the solution to remove caustic lime which is sometimes present in the crude commercial acetate.

J. P. L.

Estimation of Morphine. By H. Goebel (*Chem. Zeit.*, **11**, 508).—The process recommended by the United States Pharmacopœia for the estimation of morphine in opium, although one of the few processes that give reliable results, contains some faults which the author has endeavoured to eliminate. The process recommended in the Pharmacopœia is to digest 5 grams of opium in 50 to 60 c.c. of water at 50—60°, after filtration 2 to 3 grams of slaked lime is added and the mixture is again filtered after the lapse of about an hour, during which time it is frequently shaken. To 50 c.c. of the filtrate, 5 c.c. of 95 per cent. alcohol, 25 c.c. of ether, and 3 grams of ammonium chloride are added; the whole is well shaken and set aside for 12 hours or so for the morphine to crystallise out. The ether is filtered off through tared filter-papers, and the alcoholic solution treated with another 10 c.c. of ether. After the ether has been filtered off, the alcoholic solution and crystals are brought on to the filter and finally washed with 5 c.c. of water, dried at 100°, and weighed. The crystals of morphine should be soluble in 100 times their weight of lime-water. The

author draws attention to the following sources of error:—(1.) The incomplete removal of all substances soluble in ether. (2.) 5 c.c. of water are insufficient to wash both filter-papers and crystals, and, in consequence, the outer and counterpoise filter-paper contains more impurity than the inner. (3.) No allowance is made for the morphine in the mother-liquor and washings. (4.) The amount of water used in the exhaustion of the opium is insufficient in the case of opium containing 15 per cent. of morphine.

In order, therefore, to eliminate some of these sources of error the author suggests the following modifications:—5 to 10 grams of opium should be exhausted with 110 c.c. of water, and 4 to 5 grams of slaked lime added without filtration, after the lapse of an hour the mixture is filtered, 50 c.c. of the filtrate is taken for analysis and treated as above. After the first 25 c.c. of ether has been filtered off, both filter-paper and the alcoholic solution are washed with pure ether. Instead of the counterpoised filter-papers a single paper is used which has been previously treated with dilute sulphuric acid. The mother-liquor and washings are measured and an allowance of 0·01 gram morphine made for every 10 c.c.

The filter-paper and crystals finally are well washed with water, dried at 100°, and weighed. The weight of the filter-paper is determined after removal of the morphine with dilute sulphuric acid and water. J. P. L.

Morphine Reaction. By G. Vulpius (*Arch. Pharm.* [3], **25**, 256—257).—Donath (Abstr., 1886, 899) has given a test for morphine founded on the simultaneous action of sulphuric acid and potassium arseniate. Sodium phosphate can be employed in like manner. Some drops of a solution containing at least 0·00025 gram of a morphine salt is placed in a porcelain dish and six drops of sulphuric acid is added, together with some centigrams of sodium phosphate; on warming and agitating the mixture, a violet colour appears when fumes begin to come off. If the heating is continued, the colour passes to brown. On adding water to the cooled mixture drop by drop, a bright red colour appears, which becomes dirty green when 3 to 5 grams of water have been added. On now shaking with an equal volume of chloroform, the latter separates out with a beautiful blue colour. The blue colour produced by ferric chloride in morphine solutions is not taken up by chloroform. J. T.

Test for Narceïne. By P. C. Plugge (*Arch. Pharm.* [3], **25**, 425—427).—Dilute sulphuric acid poured on a trace of narceïne in a porcelain dish produces no change; but when, by heating on the water-bath, the acid is sufficiently concentrated, a splendid, violet-red colour appears which becomes cherry-red on long heating. If, after cooling, a trace of nitric acid or potassium nitrite is added to this red liquid, blue-violet stripes appear therein. This is characteristic of narceïne. With traces of papaverine, morphine, and codeïne, the liquid remains quite colourless; when relatively large quantities of these bases are present, morphine and codeïne give to the acid at the most only a faint rose-red tint. Thebaïne gives a greenish-yellow to

brown colour, and narcotine a red to reddish-brown. This reaction indicates also that some of the opium alkaloïds, by this slow concentration of the sulphuric acid, afford different colour changes from those obtained by the direct addition of concentrated acid. Andromedotoxime gives a similar red colour, but this substance also becomes red on evaporation with 25 per cent. phosphoric acid, and with dilute hydrochloric acid, whilst narceïne remains colourless with these acids. Impure aconitine gives the red colour, but also gives it with dilute phosphoric acid. J. T.

Thallin. By G. Dragendorff and E. Blumenbach (*Chem. Centr.*, 1886, 874).—The characteristic reaction of this alkaloïd, the bright green coloration with ferric chloride, is well marked with solutions of $\frac{1}{10000}$, and recognisable at a dilution of $\frac{1}{100000}$. Auric chloride gives a similar and equally sensitive reaction.

For the isolation of the alkaloïd from solutions such as animal fluids, the authors suggest a preliminary treatment with light petroleum before alkalising; the alkaloïd is then exhausted by shaking with benzene after adding excess of ammonia. It was found that from a solution of 1 mgrm. in 100 c.c. of urine, a quantity sufficient for identification could be isolated by this treatment.

The results of the physiological investigation of the alkaloïd are given in the original. C. F. C.

Estimation of Indigo in Textile Fabrics. By A. Renard (*Bull. Soc. Chim.*, **47**, 41—42).—10 grams of the dyed fibres are treated in a flask with 200 c.c. of a solution made by adding 2 litres of water and 100 c.c. of milk of lime to 100 c.c. of a solution of neutral sodium hyposulphite prepared from a solution of hydrogen sodium sulphite of 35° Baumé. The mixture is heated to from 60—70°, a stream of coal-gas being passed through the flask during the reduction, and when all the colour has disappeared, a portion of the solution is decanted, cooled, its volume measured, the indigo-blue precipitated by the addition of hydrochloric acid, and, after remaining 12 hours, collected on a small filter, washed, dried, and then dissolved with the filter-paper in about 10 c.c. of fuming sulphuric acid, and the solution titrated by Müller's method. A. P.

Determination by Titration of the Free Acid in Tannin Liquor. By R. Koch (*Dingl. polyt. J.*, **264**, 395—405).—This method is based on the fact that on treating tannin liquor with albumin, and nearly neutralising the mixture with standard alkali, a light-coloured filtrate is obtained which assumes a dark colour as soon as the point of alkalinity is reached. The mode of procedure is described in detail in the original paper, and the results of several test analyses are given. The numbers obtained do not, however, agree in all cases with those yielded by Kohnstein and Simand's precipitation process (Abstr., 1885, 935). The latter is, in the opinion of the author, not wholly free from error, owing to the formation of sparingly soluble basic salts of magnesium. D. B.

New Method for the Estimation of Tannin. By Villon (*Bull. Soc. Chim.*, 1884, **47**, 97—102).—The solution of tannin is diluted to such a strength that 100 c.c. will contain about 2 grams of tannin; a solution of lead acetate is prepared by dissolving 100 grams of that salt and 20 grams of sodium acetate in a litre of water. 100 c.c. of the tannin solution is then mixed with 100 c.c. of the solution of lead acetate, allowed to remain for five minutes, and the precipitate filtered off. The specific gravity D of the solution of lead acetate is taken, and the specific gravity D′ of the tannin solution, and finally the specific gravity δ of the filtered mixture. From these data the tannin in the original solution is calculated according to the formula $\left(\frac{D + D'}{2} - \delta\right)A = \Sigma$, in which A is a constant factor whose value is experimentally determined, and varies for different kinds of tannin.

The results obtained by this method are very satisfactory, and matters contained in tanning solutions which are absorbed by skin, but which have no tanning action are not precipitated. A. P.

Estimation of Albuminoïds in Liquids from Cysts, &c. By L. Garnier (*J. Pharm.* [5], **15**, 459—461).—The author criticises a method described by G. Dumonthiers (*J. Pharm.*, 1 Dec., 1886), and would modify it so that it becomes as follows:—The liquid under examination is diluted with 5 or 6 volumes of water, neutralised with acetic acid, and subjected to a current of carbonic anhydride. The precipitate formed is collected on a tared filter and treated with a 5 per cent. solution of sodium chloride, which dissolves the globulins. The residue is coagulated at 110°, washed with water, alcohol, and ether, then dried at 105°, and weighed. This represents the caseïn or alkaline albuminate. A certain volume of the original liquid, freed from fibrin, is saturated in the cold with magnesium sulphate. The precipitate is filtered, and consists of caseïn and globulin. The amount of the latter is obtained by subtracting from the total weight that of the former previously found. The solution of globulins in sodium chloride obtained above may be employed for the qualitative analysis of the globulins as follows:—(*a*) One-third of the liquid carefully heated on the water-bath gives a precipitate of fibrinogen at 56—60°. The filtered liquid, when heated at 75—80°, deposits serum-globulin in its turn; (*b*) a second third of the liquid treated with an equal volume of a saturated sodium chloride solution generally gives no precipitate if only serum-globulin is present; whereas fibrinogen becomes insoluble; (*c*) finally the addition to the globulin solution of Schmidt's fibrin ferment determines the production of insoluble fibrin at the expense of the fibrinogen only. J. T.

General and Physical Chemistry.

Fluorescence of Manganese and Bismuth. By L. de Boisbaudran (*Compt. rend.*, **104**, 1680—1685; see also this vol., pp. 3, 4, and 189). The author has investigated the behaviour of (1) two solid solvents, and an active substance giving fluorescence with each of the solvents, as represented by mixtures of cadmium, zinc, and manganese sulphates, and calcium, magnesium, and manganese sulphates; (2) two solvents and an active substance giving fluorescence with only one of them, as represented by mixtures of barium, calcium, and manganese sulphates; (3) two solvents behaving towards each other as moderately active substances, and an active substance which fluoresces brilliantly with one only of the solvents, as represented by zinc, calcium, and bismuth sulphates, and calcium, cadmium, and bismuth sulphates.

In the first case, the effects of the two solvents are practically equal when they are mixed in the proportions of their molecular weights. In the other cases, the presence of the indifferent substance reduces the brilliancy of the fluorescence, but the latter is still distinctly recognisable, even when the proportion of the active substance is very small. C. H. B.

Variations in the Absorption-spectra of Didymium Salts. By H. Becquerel (*Compt. rend.*, **104**, 1691—1693).—The results previously obtained (this vol., p. 537) indicate either that ordinary didymium is a mixture of a large number of elements, or that its compounds as usually obtained are mixtures of the salts and sub-salts of a smaller number of elements in different states of oxidation.

The absorption-spectra of dilute solutions of different compounds of didymium differ but little, whilst the absorption-spectra of the same substance in a crystallised condition are very different. When the water and acid of a hydrated didymium salt are gradually driven off by heating, a series of products is obtained, some of which are transparent, whilst others are pulverulent or opaque, but all of them show absorption-spectra by reflection, and these spectra consist of very different bands. A table is given showing the principal absorption-bands of different didymium-compounds prepared in the way described.

In the spectra of the products obtained by successive alterations of the same compounds, there are series of bands, which are transferred from one spectra to another in such a way that the variations in the number of luminous vibrations or the inverse squares of the wave-lengths of corresponding bands are sensibly constant for each series. Each spectrum shows several of these series of bands with constant differences. The bands characteristic of several of these compounds coincide with the variable bands in the spectra of the crystals (*loc. cit.*). C. H. B.

Orthochromatic Photography. By C. H. Bothamley (*J. Soc. Chem. Ind.*, **6**, 423—433).—It is well known that gelatino-bromide plates, that is, plates coated with a dry film of an emulsion of silver bromide in gelatin, fail to give photographic representations of coloured objects with correct gradations, or in other words, with their proper degrees of relative brightness. They show a maximum sensitiveness to blue and violet, are much less sensitive to green, and are only affected by yellow, orange, and red when prepared by special methods, and when the exposure to light is greatly prolonged, whereas the eye is most sensitive to yellow, less sensitive to green and orange, and only slightly sensitive to blue, violet, and red. The term "orthochromatic" photography denotes the photographic representation of coloured objects in monochrome with correct gradations, and it is obvious that in order to attain this end the character of the plates must be altered in such a way that the sensitiveness to yellow, orange, and green is greatly increased, whilst the sensitiveness to blue and violet is reduced.

Vogel (*Ber.*, **6**, 1302) discovered in 1873 that the addition of certain dyes, such as corallin, to sensitised collodion films, made them highly sensitive to yellow or greenish-yellow rays, and this observation was confirmed and applied in photographic practice. In 1883 Attout and Clayton patented the application of eosin to gelatin plates, and their observation has since been confirmed and greatly extended by other observers, and the application of dyes to photographic plates has become of great practical importance. Eder has investigated the effect of a large number of dyes (*Sitzungsb. d. Kais. Akad. der Wissensch.*, Vienna, 1884, 1885, 1886; see also Abstr., 1885, 703; 1886, 405, 497, 958). Very few are found to exert any useful sensitising action. Cyanin and some of the eosin dyes produce the greatest effect, whilst naphthol-blue, the neutral blue of the *Frankfort Anilin-Farben-Fabrik*, and coeruleïn S. are remarkable, because they render the plates sensitive without interruption to the entire length of the spectrum from λ 3600 to λ 7600. The dyes are either added to the melted emulsion before it is poured on the plate, or the dried plates are immersed in dilute solutions of the dyes and again dried. The curves representing the action of the prismatic spectrum on plates thus prepared show two maxima, one in the blue, corresponding with the ordinary sensitiveness of the gelatino-bromide, the other in the less refrangible half of the spectrum, representing the sensitiveness due to the presence of the dye. This second part of the curve corresponds but does not coincide with the absorption-band in the spectrum of the dye (Abstr., 1886, 958). Between the two maxima there is a region of minimum action, which is generally in the green, and when the exposure to light is short the effect of this part of the spectrum is inappreciable, and the action is represented by two detached curves, one in each half of the spectrum.

Different commercial samples of the dyes have been found to produce very different effects, and the author has compared a number of samples of dyes of the eosin-group by examining their absorption-spectra, &c. The chief eosin colours are eosin, phloxin, erythrosin, and rose Bengal, which are the sodium or potassium salts of tetra-

bromfluoresceïn, dichlorotetrabromfluoresceïn, tetraiodofluoresceïn, and dichlorotetraiodofluoresceïn respectively, the different commercial varieties being distinguished by letters. Eosin A, eosin JJ, eosin VE, and eosin SGF, were found to be practically identical. Erythrosin, erythrosin extra, erythrosin I, and erythrosin RE, are also identical, and rose Bengal is indistinguishable from rose Bengal B. The samples of phloxin on the other hand were found to be variable in their properties. Erythrosin B (Casella and Co.) seems to be a mixture of eosin with either the true erythrosin or rose Bengal, and erythrosin BE is really rose Bengal. One sample of erythrosin lost 8·8 per cent. at 115—120°, whilst another lost 12·5 per cent. Attention is called to the relation between the optical properties of these dyes and their molecular weights. The absorption-band becomes narrower, more intense, and less refrangible, the fluorescence rapidly diminishes, and the tint of the dye becomes bluer as the molecular weight increases. Fluoresceïn and eosin are brilliantly fluorescent; erythrosin and rose Bengal do not fluoresce at all.

The effect of the prismatic spectrum was also investigated. Commercial dry plates were immersed for two or three minutes in water, and then for two minutes in a solution of 1 part of the dye in 10,000 parts of water, and allowed to dry in the dark; others were immersed for two or three minutes in strong ammonia diluted with 100 vols. of water, and then for two minutes in a solution of the dye (1 : 10,000) to which 1 per cent. of ammonia solution had been added. Plates prepared in this way were exposed to the prismatic spectrum of light from burning magnesium, the same length of ribbon being burnt for each exposure. This source of light was selected because it contains a very high proportion of rays of high refrangibility which tend to correct the known defect of the prismatic spectrum, that is, the abnormal extension of the more refrangible rays. When a sufficient length of magnesium ribbon is burnt at a uniform rate, the effect of inequalities is eliminated and a practically constant unit of exposure is obtained. The exposed plates were developed with alkaline pyrogallol in the usual way, and the results are expressed in the form of curves. The general character of Eder's results is confirmed, but important differences of degree were observed. Each curve has two maxima separated by a region of minimum action. Eosin in aqueous solution exerts a comparatively slight though distinct sensitising action, and with commercial phloxin the effect is slightly greater. Erythrosin produces by far the greatest effect of the dyes of this group, and rose Bengal is much superior as a sensitiser to eosin, although inferior to erythrosin. The maximum effect of erythrosin and rose Bengal is exerted somewhat on the more refrangible side of D. Cyanin differs from eosin, &c., in that it sensitises for yellow, orange, and orange-red, instead of for greenish-yellow and yellow, the maximum action being exerted between D and C. The results with this dye entirely confirm those previously obtained by Eder and by Schumann. When ammonia is applied with the dye the magnitude of the sensitising action is increased, and extends to a greater distance on either side of the maximum, thus tending to obliterate the region of minimum action. The difference between the effect of

aqueous and ammoniacal solutions is greatest in the case of eosin, but even in presence of ammonia this dye produces less effect than aqueous erythrosin. Erythrosin in presence of ammonia is the most efficient sensitiser that has yet been suggested. The most important result obtained, however, is that plates dyed with aqueous or ammoniacal erythrosin, ammoniacal rose Bengal, or ammoniacal cyanin, *are more sensitive to the yellow or orange-yellow of the prismatic spectrum than to the blue and violet*, and this even with a source of light which is extremely rich in rays of high refrangibility. When burning magnesium is the source of light, plates dyed with aqueous erythrosin or ammoniacal rose Bengal are about half as sensitive again to the yellow as to any part of the blue or violet; plates dyed with ammoniacal erythrosin are somewhat more than twice as sensitive to yellow as to blue or violet; plates dyed with ammoniacal cyanin are about half as sensitive again to orange as to blue or violet. The difference between these results and those of Eder is probably due to the fact that in most of the latter's experiments the dye was added to the melted emulsion, and the bath solutions used were weaker than those employed by the author.

At present it is not possible to explain why these dyes act as sensitisers whilst others do not. No connection can be traced between the physical and chemical properties of the dyes and their sensitising action. Eder has shown (*loc. cit.*) that the dyed silver gelatino-bromide shows an absorption-band identical in position with the sensitising effect, this band being somewhat less refrangible than the absorption-band of the dye alone or mixed with gelatin, owing to the presence of the dense silver bromide. Eder has also found that when the dye is once added to the silver bromide it cannot be removed by prolonged washing, and he concludes that the dye forms a molecular compound with the silver salt, which is decomposed by the rays which it absorbs. Some experiments by Abney indicate, however, that the dye is first decomposed by light, and the products of its decomposition reduce the silver salt when the developing solution is applied. The author points out that the dyes which exert the greatest sensitising action contain a number of atoms of bromine or iodine, have a very high molecular weight, and a complex molecular constitution, and he suggests that the weight and complex structure of the molecules may confer upon them the power of entangling and arresting the ether waves to a greater extent than lighter and simpler molecules.

For practical purposes the results with the spectrum must not be interpreted too literally. The difference between the brightness of pigments is never so great as between the brightness of the corresponding colours of the spectrum, and, moreover, all coloured objects reflect more or less unaltered white light which tends to reduce the contrasts due to differences in colour. The curve representing the action of the spectrum on plates dyed with ammoniacal erythrosin approximates to the curve representing the action of the spectrum on the eye, and this dye is the most useful sensitiser for general purposes. In order to obtain correct gradations it is necessary to reduce the intensity of the blue and violet rays, to which the plates remain very

sensitive, and this is done by interposing a transparent yellow screen between the object and the lens. The depth of tint of the screen determines the proportion of blue and violet cut off, and thus affects the result. With gas or lamp light a yellow screen is unnecessary.

The author has photographed various coloured objects, such as pottery, flowers, paintings, and landscapes, with plates prepared with ammoniacal erythrosin by the method described above, and by a slightly different method previously recommended by Mallman and Scolik (*Photo. Journal*, 1886). With ordinary plates, even under the most favourable conditions, yellow, orange, and red are represented as almost black, whilst green is far too dark, and blue and violet are practically white. With the dyed plates without any yellow screen, yellow, green, and orange are more satisfactorily rendered, but blue and violet remain far too light. When, however, the dyed plates are used with a yellow screen before the lens the results are very satisfactory; yellow objects come next to white in brightness, and the other colours are represented in their proper gradations. The plates are, however, deficient in sensitiveness to red. In landscape work, in addition to the better rendering of foliage, &c., a great advantage is gained by the fact that the yellow screen cuts off the blue atmospheric haze. The interposition of the screen of course necessitates a longer exposure.

Dyed plates have already been largely employed, with great advantage, in the reproduction of pictures, and are also found to be valuable in micro-photography and in stellar photography. Hasselberg, of Pulkowa, has used dyed plates with success in photographing the less refrangible end of the spectrum, and he recommends the following solutions, which are applied to the plates after the latter have been immersed in dilute ammonia:—*from* C *to* λ 5600; alcoholic cyanin solution 1 : 400, 2 parts; ammonia 1 part; water 100 parts: *from* λ 5600 *to* F; chrysaniline solution (1 : 1000) 3 parts; eosin solution (1 : 1000) 5 parts; ammonia 1 part; water 100 parts. Eosin sensitises for yellowish-green and chrysaniline for green. C. H. B.

Conductivity of Mixtures. By E. Bouty (*Compt. rend.*, **104**, 1699—1702).—The author explains certain methods of calculating the conductivity of dilute solutions of mixed salts from the known conductivity of its constituents. The methods and results will be more fully developed in a subsequent paper. C. H. B.

Phosphates of the Alkaline Earths. By Berthelot (*Compt. rend.*, **104**, 1666—1667).—A note on a recent paper by Joly.

Trimetallic Phosphates. By A. Joly (*Compt. rend.*, **104**, 1702—1705).—The formation of the colloidal modification of sodium strontium phosphate (this vol., p. 637) from trisodium phosphate and strontium chloride develops +15·3 Cal., whilst the formation of the same salt in the crystalline condition, $NaSrPO_4 + 9H_2O$, develops +50·4 Cal. When free from sodium chloride, the crystals are very slightly decomposed by cold water. Decomposition takes place more

rapidly at 20°, and at about 70° the double salt splits up into trisodium phosphate and tristrontium phosphate.

When strontium chloride solution is poured into a solution of trisodium phosphate at about 10°, a gelatinous precipitate of tristrontium phosphate is first formed with absorption of heat, but this rapidly changes into crystalline sodium strontium phosphate with development of heat. The rapidity with which crystallisation takes place is doubtless due to the presence in the gelatinous precipitate of a small quantity of colloidal sodium strontium phosphate, which rapidly becomes crystalline, and thus initiates the transformation of the entire mass.

Sodium strontium arsenate (*loc. cit.*) is more stable than the corresponding phosphate; heat of formation in the crystalline condition, +50·2 Cal.

The author was unable to obtain any evidence of the existence of a double sodium calcium phosphate between 10° and 18°.

The corresponding crystalline double phosphate and double arsenate of barium can, however, be readily obtained in a similar manner; their heats of formation are respectively +50·8 Cal. and +50·4 Cal.

Sodium barium phosphate is less stable than the strontium compound. It is more readily decomposed by water, and the tendency to form barium triphosphate is greater. The latter compound seems to exist in a peculiar molecular condition.

The phenomena observed in the case of sodium strontium and sodium barium phosphates are similar to those previously observed with ammonium magnesium phosphate. C. H. B.

Heat of Combustion of Organic Compounds. By F. Stohmann (*Ber.*, **20**, 2063—2066).—A reply to Thomsen (this vol., p. 761), in which the author discusses the difference between his results and those of Berthelot and Vieille, and points out that the differences are in the majority of cases less than is indicated by Thomsen.

W. P. W.

Heat Equivalents of Benzoyl-compounds. By F. Stohmann, P. Rodatz, and W. Herzberg (*J. pr. Chem.* [2], **36**, 1—16).—In the following determinations, the substances were burned in free oxygen; the substance was put into a small lamp, which in the case of compounds which melt with difficulty was provided with platinum wires, to conduct the heat from the wick to the substance. Several experiments made with each substance gave the following mean results:—

	Heat equiv. per gram-mol.	Heat of formation.
Benzoic acid	770467	94533
„ anhydride	1556185	104815
Benzaldehyde	841746	23254
Benzyl alcohol	895267	38733
Methyl benzoate	943976	84024
Ethyl „	1099307	91693
Propyl „	1255010	98990

	Heat equiv. per gram-mol.	Heat of formation.
Isobutyl benzoate	1411972	105028
Amyl „	1570048	—
Phenyl „	1505196	61804
Paracresyl benzoate	1660990	69010
Orthoxybenzyl benzoate.....	1815232	77768
Pseudocumenyl „	1968760	87240
Thymyl „	2131314	90480
Resorcinyl „	2238402	124598

The difference in heat equivalents of benzene (*J. pr. Chem.* [2], **33**, 257) and benzoic acid is −9063 cal. This number is also obtained by adding together the differences in the heat equivalents shown in the conversion of toluene to benzyl alcohol, benzyl alcohol to benzaldehyde, and benzaldehyde to benzoic acid, and subtracting from the whole the heat equivalent of toluene less that of benzene.

The conversion of benzoic acid and the formation of benzoic ether are enthodermic processes; the mean difference in the case of the alkyl ethers (obtained by comparison of the heat equivalents of benzoic acid and alcohol on the one hand, and the heat equivalent of the salt on the other) is −4740 cal. In the case of the aromatic benzoates the mean difference is −10833 cal. (compare this vol., p. 427).

N. H. M.

Relation between the Boiling Points of the Monatomic Alcohols and their Constitution. By F. Flawitzky (*Ber.*, **20**, 1948—1955).—The relation between boiling points and the constitution of monhydric alcohols is discussed, and several tables given. The author considers that although it is not yet possible to show a general dependence of the boiling points on the constitution of alcohols, it is possible to predict approximately a boiling point when the constitution is known.

N. H. M.

Alteration of the Freezing Point. By F. Kolácek (*Ann. Phys. Chem.*, **31**, 526—536).—In these remarks on Helmholtz' paper on this subject, the author defines the freezing point of a salt solution as the temperature at which the ice and salt solution have the same vapour-tension, and points out that this definition was not put forward as a shrewd conjecture, as Helmholtz supposes, but was the result of general reasoning. The formula given for the freezing point is extended to the case when the heat of solution comes into play. From thermodynamic considerations he finds that—

$$\left[\log \frac{p_w}{p}\right] = \left[\log \frac{p_w}{p}\right]_{T_1} + \frac{s}{RA}\int_{T_1}^{T_1} V \frac{dT}{T^2},$$

where T, T_1 are arbitrary temperatures, p_w, p the vapour-tensions of water and the salt solution, s the amount of salt dissolved.

If s be small, we see that $\log \frac{p_w}{p}$, and therefore $\frac{p_w - p}{p_w}$, is independent of T, a law which has already been discovered by Wüllner.

If $T = 273 - t$ be the freezing point, since (*Ann. Phys. Chem.*, **29**, 349)

$$\log \frac{p_e}{p_w} = - t0{\cdot}00965(1 + t\,0{\cdot}000531 \ldots),$$

we find the equation

$$0{\cdot}00965t(1 + t\,0{\cdot}000531) = \left[\log \frac{p_w}{p}\right]_{T_1} + \frac{s}{RA}\int_T^{T_1} \frac{dT}{T^2} V.$$

Since V is an unknown function, it might be supposed that the best course would be to take $T = T_1$ when the term under the integral sign vanishes, but the values of $\log p_w/p$ below zero are unknown. The next best thing to do is, make this term a minimum.

The present research gives $\frac{dt}{dp}$: R, a, b are known constants, and v may be calculated from the formula $p + a/v^2 = RT/(v - b)$. The ratio c_p/c_v is known, and c_p has been found by Wiedemann. On substitution, ψ turns out to be very nearly constant. Thus integrating the equation

$$f - t\left(\frac{df}{dt}\right)_v c/v^2,$$

we find $$f = F(t)/v^2 + t\phi(v).$$

Clausius chooses $\phi(v) = 0$, $F(t) = 1/t$, Van der Waals $\phi(v) = 0$, $F(t) = 1$. Both choose the form of f, so as to satisfy the above equation. The present experiments, conducted at one temperature, afford no information about the form of $F(t)$. We are therefore unable to discriminate between the hypotheses of Clausius and Van der Waals on this point, though the formula of Clausius gives results most in accordance with the numbers obtained from the experiment, unless the value of a be altered. C. S.

Cooling of Carbonic Anhydride on Expansion. By E. Natanson (*Ann. Phys. Chem.* [2], **31**, 502—526).—The author believes that fresh measurements of the internal work of an expanding gas may supply considerable information about the forces which act between the molecules. The method adopted was the same in principle as that used by Thomson and Joule. The gas was allowed to expand through a porous plug of cotton-wool. Greater care was taken to secure the purity of the gas. This is most essential, for Thomson has pointed out that mixtures of gases behave in a very anomalous manner.

Carbonic anhydride was chosen as the subject of experiment, because the intermolecular forces are large, and the many previous researches supply the requisite data for the calculations.

The gas contained in a strong iron bottle escaped into a sphere (used for the purpose of equalising the pressure), and passed through a series of drying tubes filled with calcium chloride, into a number of copper tubes immersed in a water-bath of very considerable capacity. To increase the effective surface of the tubes, they were filled with

metal turnings. Thus the gas on entering the nozzle containing the porous plug was at a uniform temperature equal to that of the water-bath. The nozzle was of exactly the same construction as the one employed in the experiments of Thomson and Joule. By means of stopcocks placed between the sphere and the plug and at the extremity of the nozzle, the pressure on each side of the plug could be completely controlled. Fifty-three experiments were made at pressures ranging from 2 to 25 atmospheres, with the gas at a mean temperature of 20° C. If ΔT, Δp be the differences of temperature and pressure on the two sides of the plug, the results of the experiments show that at a temperature of 20° C.,

$$\frac{\Delta \mathrm{T}}{\Delta p} = 1{\cdot}18 + 0{\cdot}0126p,$$

p being the mean of the pressures on the two sides of the plug, measured in atmospheres.

Taking the equation of elasticity to be

$$p = \mathrm{R}t/(v - b) - f(v, t),$$

an attempt is made to determine the form of the function f. Applying the laws of thermodynamics to the present case of a gas expanding through a porous plug under small differences of pressure, we find

$$0 = c_v dt + \left\{ t\left(\frac{dp}{dt}\right)_v - p \right\} dv + d(pv),$$

which, in virtue of the equation of elasticity, may be reduced to

$$v^2\left\{ f - t\left(\frac{df}{dt}\right)_v \right\} = v^2\left\{ -\left(c_v \frac{dt}{dp} + v\right)\frac{dp}{dv} - p \right\}.$$

Since it is our object to calculate merely the numerical value of the right hand side of this last equation, we may use Van der Waals' formula, $p = \mathrm{R}t/(v - b) - a/v^2$, which is known to give the compressibility correctly. Expressing $\frac{dp}{dv}$ by this means in terms of $\frac{dt}{dp}$ we arrive, on substitution, at a result of the form

$$v^2\left\{ f - t\left(\frac{df}{dt}\right)_v \right\} = \psi\left(\frac{dt}{dp}, c_v, \mathrm{R}, a, b, v\right),$$

where ψ is a known function.

Put $$x = \left[\log \frac{p_0}{p}\right]_{\mathrm{T}_1},$$

and $$y = \frac{s}{\mathrm{RA}}\int_{\mathrm{T}}^{\mathrm{T}_1} \frac{d\mathrm{T}}{\mathrm{T}^2}\,\mathrm{V}.$$

Then approximately

$$0{\cdot}000965t = x + y.$$

Remembering that t is constant with respect to T, we see that when

y is a minimum; s a maximum, and *vice versâ*. Supposing y positive, the required values of T_1 may be found by plotting the curve ordinate and abscissa T_1, x, and selecting by inspection the least maximum value of x. Then neglecting y, we obtain from the last equation a near approximation to the value of t, the temperature of the freezing point. A table of the values of this quantity for some 20 substances is given. The greatest difference between theory and observation is about 17 per cent., a great improvement on the values given by Helmholtz, for which the discordance is as much as 40 per cent. in several cases. C. S.

Phosphonium Chloride. By S. Skinner (*Proc. Roy. Soc.*, 1887, 283—289).—In order to determine the relations of phosphonium chloride to temperature, volume and pressure, the author compresses equal volumes of phosphine and hydrogen chloride in a Cailletet's apparatus. The critical point was found at 48° under 95 atmos. The maximum vapour-pressure line lies below those of hydrogen chloride and phosphine at all temperatures. From −30° to 10° it is normal; above this combination begins. At temperatures near the critical points the volume of liquid phosphonium chloride produced is nearly one-half of that of the constituents (liquid). H. K. T.

Apparatus for Determining Vapour-densities. By C. Schall (*Ber.*, **20**, 1827—1830).—A modification of the apparatus lately described by the author (this vol., p. 695).

Determination of the Vapour-density of High-boiling Substances under Diminished Pressure. By C. Schall (*Ber.*, **20**, 2127—2129).—An application of the form of manometer employed by Meier and Crafts (*Ber.*, **13**, 851), and by Nilson and Pettersson (*ibid.*, **17**, 987) to the apparatus described by the author (preceding Abstract). Results obtained by its use are given in the paper. W. P. W.

Influence of Temperature on the Rapidity of the Action of certain Mineral Acids on Marble. By W. Spring (*Bull. Soc. Chim.*, **47**, 927—933).—The rapidity of action of hydrochloric, hydrobromic, hydriodic, nitric and perchloric acids on marble increases with the temperature, it being about doubled for a difference of every 20° between 15° and 55°.

When an aqueous solution of one of the above acids is allowed to act on marble until action ceases, the author finds that the rapidity of action decreases uniformly with the strength of the acid until three-fifths of the acid has been neutralised; after this point, the decrease of the rapidity of action is rather less than the decrease in the amount of acid present; this bears out the observation of Ostwald, that the rapidity of the action of monobasic acids is increased by the presence of their salts. A. P.

Application of the Electrometer to the Study of Chemical Reactions. By E. Bouty (*Compt. rend.*, **104**, 1789—1791 and 1839—1841).—An application of the measurement of resistances to determine

the effect of mixing solutions of potassium sulphate and sulphuric acid. The observed resistance is greater than that calculated on the supposition that there is no action, and it follows that the normal salt combines with the acid to form potassium hydrogen sulphate; as the solution becomes more and more dilute the quantity of potassium hydrogen sulphate diminishes, and eventually it is completely converted into the normal salt. The molecular resistance of the acid sulphate varies according to the same law as that of other salts; that is to say, it is proportional to a factor $1 + Km^{\frac{1}{3}}$, and the proportion of the acid salt in a solution is given by the expression $y = Ym^{\frac{1}{3}}$. The dissociation of the acid salt is indicated by the somewhat high value of $m^{\frac{1}{3}}$ in the formula for the molecular resistance.

Assuming that the molecule of potassium hydrogen sulphate constitutes a single electrolytic molecule, its resistance at the limit will be equal to that of the normal salt, and in solutions containing not more than 0·1 gram-equivalent per litre, the difference between the resistances of the two salts will be negligeable compared with the much greater conductivity of the free acid. Calculating from the observed resistances of the liquid, it is found that the proportion of the acid sulphate increases with the temperature, and, combining this with the previous result, it follows that potassium hydrogen sulphate is more stable in warm and concentrated solutions. At the same temperature and with the same degree of concentration, the proportion of the acid salt increases with an increase in the relative proportion of either the free acid or the normal salt, an excess of the normal salt being more favourable to this change than an excess of sulphuric acid. These results agree with the results of Berthelot's thermochemical measurements.

It is possible that the great variations in the resistances of abnormal salts and of free acids may be due to the progressive dissociation of complex electrolytic molecules, according to the same law as the dissociation of potassium hydrogen sulphate. This effect will be added to, but will not modify the law of the variation of the resistances of salts which are normal in all degrees of dilution. C. H. B.

Decomposition of Thiosulphates by Acids. By G. Foussereau (*Compt. rend.*, **104**, 1842—1844).—The decomposition of thiosulphates by acids was investigated by measuring the resistances of the various solutions—the rate and amount of change being measured by the increase in resistance. With solutions containing one-twelfth of a gram-equivalent of sodium thiosulphate per litre, decomposition by hydrochloric acid commences immediately and its velocity increases rapidly, then more slowly, the limit corresponding with complete decomposition. With very dilute solutions, containing only 0·001 to 0·0005 gram-equivalent per litre, decomposition likewise commences immediately, but is at first very slow. The rate of change accelerates gradually during the first few days, attains a maximum in about 40 days, and then the change becomes less rapid, and finally ceases when decomposition is complete. The rate of decomposition is accelerated by increase of temperature and also by adding a small quantity of a similar mixture in which decomposition has taken place and which,

therefore, contains minute particles of sulphur. Under the latter conditions, the small globules of sulphur seem to act in the same way as crystals in a supersaturated solution.

When a liquid in which the decomposition is taking place is examined under a microscope, it is seen to contain very minute globules of sulphur which have a rapid Brownian movement. The reaction, however, is not due to the presence of living organisms, and takes place with equal rapidity in sterilised liquids. C. H. B.

Apparatus for Fractional Distillation under Reduced Pressure. By L. Meyer (*Ber.*, **20**, 1833—1836).—This apparatus consists of a cylindrical receptacle having four tubulures, two lateral, one at the top, and one (which terminates in a narrow tube) at the bottom. The lateral tubulures serve respectively to admit the end of the condenser and to connect the apparatus by means of a three-way tap with the air-pump. The bottom tubulure is fitted by means of a cork into the receiver. A piece of glass tubing longer than the cylinder and also connected with the pump by a three-way tap, is fitted by means of a cork (air-tight) into the upper tubulure, so that it may at will be depressed until the lower end, which is ground into the lower tubulure, completely shuts off the cylinder from the receiver. When working the lower tubulure is open, and the distillate flows into the receiver. When it is wished to change the receiver, the glass tube is depressed and the distillate accumulates in the cylinder. By means of the three-way tap on the tube air can be admitted to the receiver, and the latter taken off and replaced by a new one. This is then rendered vacuous by help of the three-way tap, and the tube raised. The accumulated distillate flows into the new receiver and the distillation and fractionation may thus be carried on without intermission. The advantage claimed for the apparatus is that by the tube-joint the usual stopcock at the lower tubulure is dispensed with.

L. T. T.

Inorganic Chemistry.

Precipitation of Mixtures of Iodates and Sulphates by Barium Salts. By Chroustchoff (*Compt. rend.*, **104**, 1711—1714).—The ultimate product of the action of barium chloride on potassium iodate is the iodate, $BaI_2O_6 + H_2O$, which readily loses water. If dried at 140° and then left in contact with a solution of potassium sulphate for 67 hours, 88 per cent. of the salt is converted into barium sulphate. The precipitates obtained by adding barium chloride to mixtures of potassium iodate and sulphate, and by the action of potassium iodate on barium sulphate, and of barium iodate on potassium sulphate, vary in composition with the time of contact, temperature, and other conditions. The recently precipitated compounds are more readily decomposed than the same compounds after drying. In all cases, the composition of the precipitates agrees with the calculations from

thermal observations. The changes are limited by the dissociation of the hydrates of barium and potassium iodates.

Freshly precipitated barium iodate, $BaI_2O_6 + H_2O$, when left in contact with a solution of potassium sulphate for 25 minutes is converted into a mixture of 61 parts of barium sulphate and 39 parts of iodate, BaI_2O_6. Freshly precipitated barium sulphate left in contact with a solution of potassium iodate for 30 minutes yields a mixture of barium sulphate, 86·5 parts, and barium iodate, BaI_2O_6, 13·5 parts.

C. H. B.

Percentage of Oxygen in Air. By W. Hempel (*Ber.*, **20**, 1864—1873).—This paper gives the results of analyses of samples of air simultaneously collected by the author in Dresden, by Kreusler near Bonn; by Morley in Cleveland, North America; by Pusinelli in Para (Belem), Brazil (lat. 1½° S.); by Schneider in Tromsöe, Norway (lat. 69½° N.). The samples were taken daily between April 1 and May 16, 1886, the times being simultaneous in all places, and corresponding to 2.12 P.M. at Bonn. Full tables of the results are given. The mean percentages of oxygen for each place were—Para, 20·92; Bonn, 20·92; Cleveland, 20·93; Dresden, 20·93; and Tromsöe, 20·95. The maximum observed was 21·00 on April 22nd at Tromsöe; the minimum 20·86 on April 26th in Para. The mean percentage of oxygen in the air as deducible from the whole series of observations is 20·93. During the time these observations were being made, the percentage of oxygen was rather greater near the pole than near the equator.

L. T. T.

Preparation of Hydrogen Sulphide free from Arsenic. By R. Fresenius (*Zeit. anal. Chem.*, **26**, 339—340).—Calcium sulphide (prepared by igniting a mixture of plaster of Paris and coal) yields the pure gas when treated with dilute hydrochloric acid. To evolve the gas in a regular stream a mixture of the calcium sulphide, with one-fourth of its weight of plaster of Paris and enough water to make a cream, is poured into shallow paper trays. As soon as it has set the cake is cut up into blocks, which are dried at a gentle heat. They are then used in a Kipp's or other gas-evolution apparatus. The stream of gas is thoroughly under control.

M. J. S.

Purification of Hydrogen Sulphide from Hydrogen Arsenide. By O. Jacobsen (*Ber.*, **20**, 1999—2001).—The method is based on the fact that hydrogen arsenide reacts violently with iodine at the ordinary temperature, arsenious iodide and hydrogen iodide being formed. A narrow tube, 30 to 40 cm. long, is loosely filled with coarsely powdered, air-dried, iodine interspersed with glass-wool. 2 or 3 grams of iodine will remove every trace of arsenic from hydrogen sulphide (prepared from the ordinary impure materials), passing over it for several days. In purifying hydrogen, the latter is subsequently passed over glass wool wetted with potassium iodide solution and then through aqueous potash.

N. H. M.

Affinity of certain Bivalent Metals for Sulphuric Acid. By R. Fink (*Ber.*, **20**, 2106—2108).—A summary of results obtained in

an investigation to determine the relative affinity of biacid metallic hydroxides insoluble in water for sulphates of metals of the same group. The method adopted was to make one-fifth normal solutions of the pure normal sulphates of the metals, and precipitate 50 c.c. of one of these solutions with 10 c.c. of normal soda solution; the moist hydroxide, after thorough washing, was mixed with 50 c.c. of water and 50 c.c. of the sulphate solution of one of the metals, and digested at 100° for three hours with continual shaking. The precipitate and solution were then analysed. A preliminary experiment was made in the case of those metals which form basic salts by treating the hydroxide in exactly the same way with 50 c.c. of the sulphate solution of the same metal; the composition of the precipitate was then determined and was found to be approximately constant and independent of the volume of the one-fifth normal sulphate solution employed. As a result, it was found that instead of containing 1 equivalent of the metal the zinc precipitate contained 1·16 eq. of zinc and 0·22 eq. of sulphuric acid; the copper precipitate 1·275 eq. of copper and 0·301 eq. of sulphuric acid, the cobalt precipitate 0·12 eq., and the nickel precipitate 0·05 eq. of the respective sulphates, whilst the hydroxides of magnesium, manganese, and iron (ferrous) remained unaltered. The hydroxides of those metals forming basic salts, with the exception of nickelous hydroxide, were digested with the sulphate solution of their respective metals, washed with water, and then similarly treated with the sulphate solution of another metal. The results of the experiments are summarised in the following table:—

Hydroxide or basic salt (*b*).	Sulphate.	Precipitate contained—
Zinc (*b*).	Copper.	The whole of the copper.
Copper (*b*).	Iron.	60·8 per cent. of iron.
Magnesium.	Iron.	71·2 „ „ „
Cobalt (*b*).	Manganese.	14·7 „ of manganese.
Nickel.	Manganese.	12·3 „ „ „
Copper (*b*).	Magnesium.	No magnesium.
Magnesium.	Nickel.	60·5 per cent. of nickel.
Iron.	Manganese.	No manganese.
Zinc (*b*).	Nickel.	Small quantity of nickel.
Magnesium.	Manganese.	71·2 per cent. of manganese.

The experiments with the ferrous salts were conducted in an atmosphere of hydrogen to avoid oxidation. W. P. W.

Sulphites. By P. J. Hartog (*Compt. rend.*, **104**, 1793—1796).—When water containing magnesium hydroxide in suspension is saturated with sulphurous anhydride, concentrated in a vacuum at a temperature below 100°, and allowed to cool, it deposits crystals of the hexhydrated magnesium sulphite, $MgSO_3 + 6H_2O$, described by Rammelsberg and Marignac. If the solution is evaporated at a high temperature, it yields crystals of the tri-hydrate $MgSO_3 + 3H_2O$,

which was prepared by Muspratt, but the existence of which has been denied. The liquid must be mixed with fragments of pumice-stone or glass in order to prevent the separation of the salt in the form of a hard crust adhering firmly to the sides of the vessel. The heats of formation of the sulphite and its hydrates were determined by dissolving them in hydrochloric acid.

$Mg + S$ solid $+ O_3 = MgSO_3$	develops	+222·92 Cal.
$MgSO_3 + 3H_2O$ solid $= MgSO_3{\cdot}3H_2O$..	„	+ 11·40 „
$MgSO_3 + 6H_2O$ solid $= MgSO_3{\cdot}6H_2O$..	„	+ 13·88 „

Ammonium sulphite, $(NH_4)_2SO_3 + H_2O$, can be obtained in the dry state by means of kaolin. It oxidises more rapidly when solid than when in solution, and therefore cannot be dried in the usual way. Heat of dissolution −4·34 Cal. The anhydrous salt, mixed with some sulphate, is obtained by evaporating the solution at a moderate temperature.

Ammonium Magnesium Sulphite.—The hydrate, $(NH_4)_2SO_3,3MgSO_3 + 18H_2O$, described by Marignac and Rammelsberg, is obtained by neutralising with ammonia a solution of magnesium sulphite in sulphurous acid, passing sulphurous anhydride into the liquid, evaporating in a vacuum till a white precipitate begins to form, filtering, and allowing to crystallise. The hexhydrate,

$$(NH_4)_2SO_3,MgSO_3 + 6H_2O,$$

is obtained by heating the preceding salt in a current of dry nitrogen at 115—120°. The salt decomposes above 125°, and cannot be obtained in the anhydrous condition. The heat of formation was determined by dissolving in hydrochloric acid :—

$3(MgSO_3 + 6H_2O) + (NH_4)_2SO_3 = (NH_4)_2SO_3,3MgSO_3,18H_2O$	absorbs	− 2·11 Cal.
$3MgSO_3 + (NH_4)_2SO_3 + 18H_2O$ solid $= (NH_4)_2SO_3,3MgSO_3,18H_2O$	develops	+39·48 „
$3MgSO_3 + (NH_4)_2SO_3 + 6H_2O = (NH_4)_2SO_3,3MgSO_4,6H_2O$.....	„	+26·18 „

It is evident that the formation of these salts is accompanied by a considerable development of heat, a result which supports Berthelot's theory of the existence of ammonio-magnesium bases which unite with acids with a greater development of heat than the bases separately. C. H. B.

Density of Nitric Oxide at 100°. By G. Daccomo and V. Meyer (*Ber.*, **20**, 1832).—The authors filled two like thermometer-tubes, the one with air, the other with nitric oxide, the surfaces of the sealing liquids being at equal heights in the tubes. The two tubes were then placed side by side and cooled in a bath of ether and solid carbonic anhydride. Observations were taken at −96° and −107°. The contraction of both gases was exactly the same, thus proving that even as low as −100°, the density of nitric oxide still corresponds with the simple formula NO. L. T. T.

Behaviour of Phosphorus, Arsenic, and Antimony at a White Heat. By J. Mensching and V. Meyer (*Ber.*, **20**, 1833).—The authors find that at a white heat the vapour-densities of phosphorous and arsenic are much less than at lower temperatures, and approach but do not quite reach those required for the formulæ P_2 and As_2.

Antimony volatilises at a white heat, and the vapour-density is lower than that required for Sb_4 or even Sb_3, but the authors are unable to say definitely whether the density corresponds with a diatomic or a monatomic molecule, as the vapour at the temperature obtained had not yet fully attained the properties of a gas. L. T. T.

Arsenic. By A. Geuther (*Annalen*, **204**, 208—225):—When a mixture of phosphorus and arsenic trichlorides is treated with water the arsenious acid first formed is rapidly reduced to metallic arsenic. Thus obtained arsenic forms a brownish-black amorphous powder of sp. gr. 3·704 at 15°. It remains unchanged and unoxidised when exposed to the atmosphere at ordinary temperatures. Arsenic thus has at least three allotropic modifications, viz., brownish-black amorphous form of sp. gr. 3·704, black amorphous form of sp. gr. 4·71, and steel-grey crystalline form of sp. gr. 5·73. Besides these, Bettendorf described (*Annalen*, **144**, 110) a yellow amorphous modification deposited on the coolest parts of the tube during the rapid sublimation of arsenic in a stream of hydrogen. The author is inclined to view this as probably an amorphous variety of still lower specific gravity. The author points out that the specific gravities of the three modifications mentioned above stand to each other in the proportion of 4 : 5 : 6, and suggests that their molecules may very likely be expressed by the formulæ $(As_4)_2$, $(As_4 + As_6)$, and $(As_6)_2$, or some multiple of these formulæ respectively.

The blackening of metallic arsenic by exposure to the air is generally ascribed to the formation of a suboxide, but the author finds that it is due to superficial oxidation to arsenious anhydride. If crystalline arsenic is finely powdered and exposed to the air it increases in weight for some time. If it is then boiled with water arsenious acid is obtained in solution and pure arsenic left, of which, on further exposure to the air, a fresh portion becomes oxidised.

Realgar, when heated with a solution of sodium sulphide, yields sodium sulpharsenate and free arsenic. It is therefore a subsulphide, and not a normal sulphide as believed by Berzelius. Sodium sulpharsenate has the formula $Na_3AsS_4 + 8H_2O$, and not $2Na_3AsS_4 + 15H_2O$ as generally given.

When realgar is heated with aqueous soda, it yields free arsenic and a normal salt of the formula $Na_6As_2O_5S_3 + 24H_2O$. This crystallises in small, colourless needles easily soluble in water. L. T. T.

Carbonic Anhydride in the Air of Schoolrooms. By W. Fossek (*Monatsh.*, **8**, 271—291).—For his determinations, the author used a modification of the Pettenkofer-Hesse method by which the air of the schoolroom can be taken by the teacher at any given time in

an unobtrusive manner, and by which the accuracy of the determinations is not influenced by the temperature and amount of carbonic anhydride in the air of the laboratory. For details of the apparatus, the description and plates of the original paper must be consulted.

The author found that an unventilated schoolroom, the air of which contained on three occasions 0·078, 0·092, 0·088 per cent. by volume of carbonic anhydride respectively before the class met, contained, after being occupied for three hours by a class of 58 scholars, 0·620, 0·637, and 0·557 per cent. by volume respectively. G. H. M.

Crystallisation of Alkalis from Alcohol. By C. Göttig (*Ber.*, **20**, 1907—1908).—The author finds that the crystals lately described by him (this vol., p. 636) as hydrates of potash contain alcohol of crystallisation. Their true composition has not yet been determined. L. T. T.

Decomposition of Sodium Thioarsenate by Silver Nitrate. By C. Preis and B. Rayman (*Bull. Soc. Chim.*, **47**, 892—896).—On adding silver nitrate to an ammoniacal solution of the sodium thioarsenate, AsS_4Na_3, silver sulphide is precipitated, and the solution contains arsenic acid, sodium nitrate, and nitric acid, the reaction taking place according to the equation—

$$AsS_4Na_3 + 8AgNO_3 + 4H_2O = 4Ag_2S + H_3AsO_4 + 5NaNO_3 + 5HNO_3.$$

When, however, silver nitrate is added to an aqueous solution of sodium thioarsenate, or if the solution contains nitric acid, silver sulphide is precipitated as before, and arsenious but no arsenic acid is found in the solution, nitric acid and sodium nitrate being formed as before. This reaction takes place according to the two following equations:—

$$(1.)\ AsS_4Na_3 + 8AgNO_3 + 4H_2O = 4Ag_2S + H_3AsO_3 + 5HNO_3 + 3NaNO_3 + O.$$

$$(2.)\ AsS_4Na_3 + 6AgNO_3 + 3H_2O = 3Ag_2S + H_3AsO_3 + 3HNO_3 + 3NaNO_3 + S.$$

The larger the amount of free acid present the more nearly does the reaction conform to equation 1, but in an aqueous solution, which is neutral at the commencement of the reaction, it conforms more closely to equation 2. The oxygen which is formed according to equation 1 is not liberated in the free state, but as the two reactions always take place simultaneously it combines with some of the sulphur thrown down according to 2, and is found as sulphuric acid. These reactions take place immediately, and are not affected by the length of time allowed for the precipitation. A. P.

Corrosion of Zinc by Ammonium Chloride and Potassium Nitrate. By J. H. Fisher (*Pharm. J. Trans.* [3], **17**, 783—785).—A solution of ammonium chloride, or one of potassium nitrate, even

when concentrated and boiling, has little action on metallic zinc. But if the two solutions be mixed, the action is marked even in the cold, and it becomes very decided on boiling, for the zinc is then quickly attacked, and ammonia, potassium nitrite, zinc chloride, and a double chloride of zinc and ammonium insoluble in water are the products. R. R.

Components of the Rare Earths yielding Absorption-spectra. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 2134—2171).—The solutions of the nitrates of the rare earths accompanying thorium in the thorite from Brevig and Arendal give absorption-spectra containing bands peculiar to didymium, samarium, erbium, thulium, and Soret's X or holmium, and a careful measurement of these shows that in both solutions each element is represented only by some of its bands, and that the wave-lengths and intensities of those observed in the solution from the first differ in some cases from those observed in that from the second mineral. For example, the band $\lambda = 428{\cdot}7$, regarded as the sixth in decreasing order of intensity of the absorption-bands of Soret's X, is the most intense X line in the Brevig thorite, and the other bands are either absent or scarcely visible, but $\lambda = 428{\cdot}7$ is scarcely visible in the absorption-spectrum of the Arendal thorite. Hence it is argued that X must consist of at least two elements, one of which gives the band $\lambda = 428{\cdot}7$, and the other the remaining absorption-bands usually ascribed to X.

The rare earths examined were obtained from the following minerals:—

Mineral.	Absorption-spectra indicated the presence of
Thorite from Brevig	Didymium, thulium, erbium, X, samarium.
,, ,, Arendal.....	,, ,, ,, ,, ,,
Wöhlerite from Brevig.....	,, ,, ,, ,,
Didymium and samarium material from cerite from Bastnäs.....	,, ,, ,,
Fergusonite from Arendal.....	,, ,, ,, ,, ,,
,, ,, Ytterby	,, ,, ,, ,,
Euxenite ,, Hitterö.....	,, ,, ,, ,, ,,
,, ,, Arendal	,, ,, ,, ,, ,,

and the method by which the material was prepared is described in each case. The fergusonite from Arendal was fractionated 12 times, the euxenite from Hitterö 43 times, and that from Arendal 12 times, and the absorption-spectra of the nitrates of the different fractions were obtained. The wave-lengths of the bands observed in the absorption-spectra of the solutions of the nitrates of the rare earths from each mineral, and their relative intensity (determined in each case in one and the same solution to render the data comparable among themselves) are given at length in tables, and for the sake of comparison the wave-lengths of the bands of the nitrates of the five earths measured by previous observers are also added.

A comparison is then instituted between the seven bands ascribed to Soret's X, and those observed in the absorption-spectrum of the nitrates of the rare earths from each mineral, or from each fraction obtained from a mineral where fractionation has been resorted to, with a result that each band is found to vary in intensity quite independently of the others. By repeated fractionation of X material, Boisbaudran has separated it into dysprosium and a new holmium, each characterised by several absorption-bands (Abstr., 1886, 667); neither of these supposed elements, however, is a simple substance, since the relative intensities of the bands of each vary in the rare earths under investigation just as they vary in the case of the parent substance X. The authors conclude that Soret's X is composed of seven distinct elements, each of which is characterised by a single absorption-band: they are, X_α, $\lambda = 640{\cdot}4$; X_β, $\lambda = 542{\cdot}6$; X_γ, $\lambda = 536{\cdot}3$; X_δ, $\lambda = 485{\cdot}5$; X_ϵ, $\lambda = 474{\cdot}5$; X_ζ, $\lambda = 451{\cdot}5$; X_η, $\lambda = 428{\cdot}5$, and are distributed in the foregoing minerals as follows :—

Mineral.	Elements.
Thorite from Brevig	X_α, X_δ, X_η.
„ „ Arendal	X_β, X_γ, X_ϵ, X_ζ, X_η.
Wöhlerite from Brevig	X_γ, X_ζ, X_η.
Cerite from Bastnäs	X_α, X_η.
Fergusonite from Arendal	X_β, X_γ, X_δ, X_ϵ, X_ζ, X_η.
„ „ Ytterby	X_α, X_β, X_γ, X_δ, X_ϵ, X_ζ, X_η.
Euxenite from Hitterö and Arendal	

Arguing in the same way from the variation in the intensity of the absorption-bands, and the presence of some and absence of others in the rare earths under investigation, the authors consider that erbium consists of two elements, Er_α, $\lambda = 654{\cdot}7$, and Er_β, $\lambda = 523{\cdot}1$; that thulium consists of two elements, Tm_α, $\lambda = 684{\cdot}0$, and Tm_β, $\lambda = 465{\cdot}0$; that didymium consists of at least ten elements, Di_α, $\lambda = 728{\cdot}3$; Di_β, $\lambda = 679{\cdot}4$; Di_γ, $\lambda = 579{\cdot}2$ and $= 575{\cdot}4$; Di_δ, $\lambda = 521{\cdot}5$; Di_ϵ, $\lambda = 512{\cdot}2$; Di_ζ, $\lambda = 482{\cdot}0$; Di_η, $\lambda = 469{\cdot}0$; Di_θ, $\lambda = 445{\cdot}1$; Di_ι, $\lambda = 444{\cdot}7$, and a tenth, Di, to which is assigned the remaining didymium bands whose intensity is too feeble to allow them to be differentiated by this method; and that samarium consists of at least two elements, Sm_α, $\lambda = 416{\cdot}7$, and a second, Sm_β, having all the remaining samarium bands, inasmuch as these could not be satisfactorily assigned to particular constituents.

In a complete table of the 40 absorption-bands observed, four bands occur which cannot be identified with any hitherto observed lines in the absorption-spectra of the rare earths; they are—

Absorption-band.	Source of rare earth.
$\lambda = 716{\cdot}4$	Fractions 8—14 of euxenite from Arendal.
$\lambda = 539{\cdot}9$	Wöhlerite and thorite from Brevig.
$\lambda = 533{\cdot}6$	Euxenite from Hitterö and fergusonite from Ytterby.
$\lambda = 488{\cdot}8$	Wöhlerite and thorite from Brevig.

Note by Abstractor.—The entire absence of any reference in this paper to the results obtained by Crookes, in his investigation of the constituents of the rare earths present in gadolinite and samarskite by comparison of the absorption and fluorescent spectra of different fractions (*Proc. Roy. Soc.*, **40**, 504; this vol., p. 334), is remarkable; inasmuch as evidence is there adduced which would show that Boisbaudran's dysprosium is composed of at least two substances, since the band $\lambda = 451{\cdot}5$ can be obtained separate from the band $\lambda = 475{\cdot}0$. W. P. W.

The Water of Crystallisation of Alums. By P. de Boissieu (*Bull. Soc. Chim.*, **47**, 494—496).—In criticising Maumené's results (Abstr., 1886, 981, this vol., p. 218), the author states that he has made a large number of very careful estimations of the water of crystallisation in potash and chrome alums, and has never been able to find more than 24 mols. H_2O, the amounts actually found varying between 23·9 and 24·1 mols.

An examination of the tensions of dissociation of normal crystallised alums and of other samples from which the water has been partially removed, seems to indicate the existence of a definite hydrated alum, containing between 7 and 16 mols. H_2O. A. P.

Chemistry of Manganese and Fluorine. By O. T. Christensen (*J. pr. Chem.* [2], **35**, 541—559).—Manganese ammonium fluoride was prepared by dissolving pure manganese oxide in hydrofluoric acid, and adding a solution of ammonium fluoride to the dilute solution. The double salt separates as a crystalline precipitate; this is treated with a dilute solution of hydrofluoric acid. When dried over sulphuric acid, it forms a homogeneous, red, crystalline powder. The methods employed in preparing the manganese oxide and hydrofluoric acid are described in detail.

In order to determine the atomic weight of fluorine, a solution of sodium thiosulphate (about 25 grams to 1 litre of water) was prepared, and the strength determined by means of iodine. A weighed amount of the double salt was put into a mixture of potassium iodide and hydrochloric acid, the whole weighed, and the sodium thiosulphate added until the solution was decolorised. The difference in weight showed the amount of sodium thiosulphate used, and from this the amount of iodine liberated by the fluorine was calculated. The results of several experiments point to the atomic weight 18·94 (H = 1) or 18·99 (O = 16). N. H. M.

Potassium Manganites. By G. Rousseau (*Compt. rend.*, **104**, 1796—1799).—When potassium permanganate (1 part) is fused for 12 hours with potassium chloride (5 parts) in a covered platinum crucible heated by a Bunsen burner, and the residue is treated with boiling water, it yields lustrous black lamellæ of the composition $K_2O,7MnO_2$. The same product is obtained from potassium manganate under similar conditions.

If the mixture of permanganate and chloride is heated for six hours at the melting point of copper, the product is $K_2O,10MnO_2$. At

an orange-red heat, with potassium chloride as a flux, the crystals formed contain 60·36—61·82 per cent. of manganese, which indicates a very high degree of condensation of the manganite. In order to ascertain if this result is due to the action of aqueous vapour on manganese volatilised with the alkaline chloride, experiments were made with a flux of potassium sulphate, which is not volatile. Under these conditions, with an open crucible, no manganite is formed, since oxygen is absorbed from the air and regenerates the manganate. If the crucible is closed, the product consists of black lustrous crystals of trimanganese tetroxide with a small quantity of an alkaline manganite.

Potassium manganite polymerises as the temperature rises, the limit being the formation of trimanganese tetroxide. This condensation is analogous to the condensation of hydrocarbons with loss of hydrogen. The manganite forms complex products, the manganese accumulating in the molecule like the carbon in the hydrocarbons, but the energy of the acid diminishes as its molecular weight increases, the change culminating in the formation of the non-acidic oxide Mn_3O_4, with elimination of the alkali.

The tendency of aqueous vapour to decompose manganates is assisted by the tendency to form potassium or sodium hydroxide. When potassium manganate is heated in a current of aqueous vapour, the product at a dull red heat consists of needles of the manganate $K_2O,7MnO_2$; at a somewhat higher temperature the product is $K_2O,8MnO_2$; at about 800°, $K_2O,10MnO_2$; after two hours at 1000°, $K_2O,12MnO_2$; after another hour at the same temperature, Mn_3O_4; and after half-an-hour at an orange-red heat, MnO. C. H. B.

Action of Sulphuric Acid on Potassium Permanganate. By B. Franke (*J. pr. Chem.* [2], **36**, 31—43).—When the green solution obtained by dissolving potassium permanganate in sulphuric acid is exposed to direct sunlight in presence of moist air, manganese heptoxide separates and then decomposes into manganese dioxide, manganese trioxide, and ozone (?), which is given off as a blue gas. The latter is insoluble in water, but disappears when brought into contact with sulphuric acid or absolute ether.

Manganese trioxide, MnO_3, is formed as a dark-red mass when the green solution of manganese oxysulphate is distilled in presence of water; it is best prepared by decomposing the green solution with potassium carbonate. The red fumes are passed into a **U**-tube surrounded by a freezing mixture in which they condense to a dark-red amorphous mass. The green solution employed should be free from manganese heptoxide. The trioxide has a peculiar odour, and volatilises at about 50° as a violet vapour, with partial decomposition into crystalline manganese dioxide and oxygen; this decomposition is complete when the substance is heated. It is sparingly soluble in water; a litre of water containing 50 mgrms. of the substance has an intense red colour. When the vapour is passed into aqueous soda or potash, alkaline manganates are produced. The reaction employed for detecting small quantities of manganese by means of potassium chlorate depends on the formation of the trioxide.

Manganic acid is formed when manganese trioxide is passed into water; it is very unstable and decomposes into manganese dioxide, oxygen, and dimanganic acid.

When cooled ether containing hydrogen chloride is treated with potassium permanganate, a dark-green solution is obtained which contains manganous manganese chloride, $Mn<^{Cl}_{Cl}>MnCl_4$. In presence of an excess of ether, the green solution is decomposed and a blue solution formed; the latter contains manganese tetrachloride. When the blue solution is saturated with hydrogen chloride, an oily green liquid containing the compound $MnCl_4(HCl)_2$, is formed (compare Christensen, this vol., p. 335). N. H. M.

Hydrochlorides of Ferric Chloride. By Engel (*Compt. rend.*, **104**, 1708—1711).—Hydrochloric acid produces no precipitate in very concentrated solutions of ferric chloride, and gaseous hydrogen chloride causes the liquefaction of the hydrates $Fe_2Cl_6 + 5H_2O$ and $Fe_2Cl_6 + 12H_2O$. These facts indicate the formation of hydrochlorides of the chloride.

When solid commercial ferric chloride is treated with a current of hydrogen chloride, it yields a liquid containing a dark-brown solid of variable composition, which may be separated by decantation or by filtration through glass-wool. If the filtered liquid is evaporated over potash in a vacuum, it yields the hydrate $Fe_2Cl_6 + 12H_2O$; if heated at 100° for several hours, it gives off hydrogen chloride, and when cooled slowly deposits large, deep garnet-red crystals of the hydrate $Fe_2Cl_6 + 5H_2O$. By this method, the pentahydrate can readily be obtained in large quantity, and constitutes an excellent material for the manufacture of officinal preparations of ferric chloride.

If the pentahydrate is treated with a current of perfectly dry hydrogen chloride, it rapidly liquefies, and when saturated with the gas at 25° and then cooled to 0°, it yields large, thin, transparent, amber-yellow lamellæ, which, when dried over phosphoric anhydride, have the composition $Fe_2Cl_6,2HCl + 4H_2O$. It is very deliquescent.

All the hydrochlorides of chlorides hitherto obtained contain water. As a rule they are more soluble than the corresponding chlorides. C. H. B.

Hydrochloride of Ferric Chloride. By P. Sabatier (*Compt. rend.*, **104**, 1849—1850).—The hydrochloride of ferric chloride, $Fe_2Cl_6,2HCl,4H_2O$, recently described by Engel (preceding Abstract), was obtained by the author six years ago (*Bull. Soc. Chim.*, 1881, 197), in the form of yellowish-brown, translucent, deliquescent lamellæ, by the action of hydrogen chloride on pentahydrated ferric chloride, or by the action of the gas at the ordinary temperature on a mixture of anhydrous ferric chloride and the pentahydrate. C. H. B.

Residues obtained from Steel and Zinc by the Action of Acids. By Osmond and Werth (*Compt. rend.*, **104**, 1800—1802).—When annealed steel is dissolved in dilute hydrochloric acid at the positive pole of a Bunsen element, it yields a skeleton of graphitoidal plates, which the authors term *cement of steel*. This residue consists

mainly of iron and carbon, but also contains water and oxygen. Tempered steel yields only a small quantity of residue, which contains comparatively little iron. The following table gives the composition of the residues from steel which originally contained 0·49 per cent. of carbon, and had been subjected to different mechanical treatment:—

	Crude.	Forged.	Tempered.
Iron	87·31	78·40	52·50
Carbon	6·78	12·00	18·90
Water	3·32	8·40	26·07
Total	97·41	98·80	97·47

The residues, especially that from tempered steel, explode when dried in a hot-air bath. When dried in a vacuum, they not unfrequently undergo spontaneous combustion. It is obvious that it is not only steel containing platinum that yields the residues first observed by Faraday.

Similar residues are obtained from impure zinc.

	Cast cold.	Cast hot.
Residue per cent.	1·63	1·19
	Composition.	
Tin	30·07	5·64
Lead	52·16	78·10
Iron	2·10	3·15
Copper	0·30	0·25
Zinc	14·85	12·04
	99·48	99·48

These residues are graphitoidal in appearance, but contain no water and are not explosive. The first corresponds in composition with the formula Pb_2ZnSn, and the second with the formula Pb_2Zn.

The conditions of cooling modify the proportion, composition, and form of the residue from one and the same alloy. C. H. B.

Paratungstates. By C. Gonzalez (*J. pr. Chem.* [2], **36**, 44—56). —The following salts were prepared from sodium paratungstate which is obtained by adding hydrochloric acid to a boiling solution of commercial sodium tungstate ($Na_2WO_4 + 2H_2O$) until slightly alkaline to litmus. The salts are sparingly soluble or insoluble, and dissolve to clear solutions in water which contains a few drops of hydrochloric acid; after some time, the solution becomes gelatinous from separation of tungstic acid.

Manganese paratungstate, $Mn_3W_7O_{24} + 20H_2O$ or $Mn_5W_{12}O_{41} + 34H_2O$, is a white amorphous powder which does not melt; after ignition, it is yellowish-green. The *cobalt salt*, $Co_3W_7O_{24} + 25H_2O$, is a bright rose-coloured microcrystalline substance which does not melt at a red heat and acquires on cooling a bluish colour. The *cadmium*

salt, $Cd_3W_7O_{24} + 16H_2O$, is a white, crystalline compound; it cannot be fused, and is orange-coloured after being heated. The *silver salt*, $Ag_{10}W_{12}O_{41} + 8H_2O$, is a whitish-yellow crystalline substance; it melts at a red heat and solidifies on cooling to a white crystalline mass with a metallic lustre. The *zinc salt*, $Zn_5W_{12}O_{41} + 37H_2O$, crystallises in white needles; when heated, it is yellow and does not melt.

The following double salts are prepared by adding a solution of the salt to a boiling solution of sodium paratungstate until the precipitate formed no longer redissolves. The solution is quickly filtered from the slight precipitate and left; after 2—3 hours, the double salt separates. *Copper sodium paratungstate*, $CuNa_8W_{12}O_{41} + 32H_2O$, crystallises in slender, bright-blue needles, melts at a red heat, and solidifies to a black lustrous mass. The *lead sodium salt*, $PbNa_8W_{12}O_{41}$ $28H_2O$, forms slender white needles; it melts at a red heat, and on solidifying forms a white mass with metallic lustre. The *cobalt sodium salt*, $Co_2Na_6W_{12}O_{41} + 30H_2O$, is a rose-coloured crystalline compound which melts at a red heat and solidifies to a black mass with a metallic lustre. The *calcium sodium salt*, $Ca_2Na_6W_{12}O_{41} + 34H_2O$, is white; it is fusible and solidifies to a black mass. The *strontium sodium salt*, $Sr_4Na_2W_{12}O_{41} + 29H_2O$, crystallises in white scales, does not fuse at a red heat, but becomes yellow. (Compare v. Knorre, Abstr., 1886, 597.) N. H. M.

Zirconium. By O. Hinsberg (*Annalen*, **239**, 253—256).—No organic zirconium-compound is produced by the action of zirconium chloride on zinc ethide. Attempts to prepare zirconium iodide by the double decomposition of zirconium sulphate and barium iodide resulted in the formation of a solution which, on evaporation over strong sulphuric acid, yielded a mixture of iodine and an amorphous powder, soluble in water, probably $ZrI(OH)_3 + 3H_2O$. Attempts to prepare zirconium iodide by passing iodine vapour over a red-hot mixture of zirconia and charcoal were also unsuccessful. W. C. W.

Reactions of Vanadic Acid. By A. Carnot (*Compt. rend.*, **104**, 1803—1805 and 1850—1853).—The estimation of vanadic acid in the form of ammonium vanadate (this vol., p. 691) can only be carried out under limited conditions.

In presence of alkaline and ammonium salts, vanadic acid is more easily estimated in the form of barium vanadate. The solution, if acid, is exactly neutralised with ammonia, heated to boiling, mixed with excess of barium chloride, agitated, and cooled quickly out of contact with air. Precipitation is complete. The precipitate is collected, washed, dried, heated, and weighed in the form of $2BaO,V_2O_5$. If the liquid which contains the precipitate is boiled, the precipitate agglomerates and becomes firmly adherent to the sides of the vessel.

A slightly ammoniacal solution of vanadic acid containing ammonium salts gives no precipitate with strontium salts. By means of this difference, vanadic acid can be accurately separated from phosphoric and arsenic acids, and, approximately, from molybdic and tungstic acids, the latter being incompletely precipitated from boiling

solutions by strontium salts. The difference can also be utilised for the accurate separation of barium and strontium. The liquid is made alkaline with ammonia, mixed with ammonium chloride and an excess of a soluble vanadate, boiled for a few minutes, and then cooled quickly out of contact with the air. The clear liquid is decanted, the precipitate washed with cold water, dissolved in hydrochloric acid, and the barium precipitated as sulphate. The strontium is precipitated by means of ammonia and ammonium carbonate.

Calcium and magnesium salts give no precipitate with dilute solutions of vanadates, but in concentrated and strongly ammoniacal solutions the vanadic acid is partially precipitated.

When an acid solution containing vanadic acid and an aluminium salt is neutralised with ammonia, the aluminium hydroxide carries vanadic acid down with it. The same result follows if the aluminium is precipitated with sodium phosphate or an alkaline sulphide. In the latter case, the presence of vanadic acid is indicated by the brown colour of the precipitate; chromium hydroxide behaves similarly, and, if in sufficient quantity, will retain the whole of the vanadium.

Vanadic acid, like phosphoric and arsenic acids, is completely precipitated by uranic salts in ammoniacal solutions, and also in presence of small quantities of free acetic acid. In order to estimate the acid in this way, the liquid is nearly neutralised with ammonia, mixed with ammonium acetate and excess of uranium nitrate, and heated to boiling. Complete precipitation is recognised by the reaction with potassium ferrocyanide. The precipitate is washed with pure water, dried, and separated from the filter-paper, which is burnt separately. The precipitate when dried at 100° has the composition

$$V_2O_5,2UO_3,(NH_4)_2O + H_2O;$$

when heated in presence of air, it loses ammonia and water, becoming $V_2O_5,2UO_3$, in which form it is weighed. Vanadic acid can be estimated by this method not only in presence of alkalis and alkaline earths, but also in presence of many metals, such as manganese, zinc, and copper, the acetates of which are not decomposed by boiling. It cannot, however, be separated by this reaction from phosphoric, arsenic, tungstic, and molybdic acids.

Ferric hydroxide carries down vanadic acid when precipitated in a solution containing it, but the vanadium can be separated by means of ammonia, ammonium acetate, or ammonium hydrosulphide, provided the precipitation is repeated several times.

Manganese forms a well-defined vanadate, by means of which both the acid and the base can be estimated with accuracy. The vanadic acid solution is mixed with a slight excess of ammonia and ammonium chloride, heated to boiling, and then mixed with ammonium chloride and manganese chloride or sulphate, boiled for two or three minutes, and cooled quickly out of contact with air. The precipitate, which is brownish-yellow and should be free from any brown oxidation-product, is collected, washed with cold water, dried and ignited. It then has the composition $2MnO,V_2O_5$. This reaction cannot be used for the separation of vanadic acid from phosphoric and arsenic acids, but it will effect a partial separation of vanadic and tungstic acids and a

very accurate separation of vanadic acid from molybdic acid. The vanadic acid is precipitated as manganese vanadate, the excess of manganese is removed by means of ammonium sulphide, and in the filtrate the molybdenum is precipitated as sulphide by adding hydrochloric acid.

In order to separate vanadic acid from its alkaline or ammoniacal solutions, it is precipitated in the form of manganese vanadate, the precipitate is dried and heated with sulphur or in a slow current of hydrogen sulphide, and the residue is treated with hydrochloric acid diluted with 15 to 20 times its volume of water, when manganese sulphide dissolves and vanadium sulphide remains undissolved.

C. H. B.

Metallic Vanadates. By A. Ditte (*Compt. rend.*, **104**, 1705—1708).—Metallic vanadates are readily obtained in a crystalline condition by adding ammonium vanadate in excess to a solution of the nitrate of the metal, this solution being hot or cold, neutral or acid, as the case may require.

Normal *magnesium vanadate*, $MgV_2O_6 + 6H_2O$, is obtained in small, transparent needles by boiling magnesium hydrocarbonate with soluble vanadic anhydride and concentrating the filtered solution in a vacuum. It loses water when heated, becomes yellow, and melts at a higher temperature. If a warm saturated solution of ammonium vanadate is mixed with excess of magnesium chloride, acidified with acetic acid and concentrated in a vacuum, it deposits brilliant red, transparent crystals of the bivanadate, $MgO,2V_2O_5 + 9H_2O$. *Barium vanadate* is obtained in colourless, transparent, anhydrous prisms, insoluble in water, by adding barium nitrate in excess to a boiling solution of ammonium vanadate. In presence of acetic acid, a red solution is obtained and, if this is concentrated, it deposits transparent, orange-red, rhombic crystals of the composition $2BaO,3V_2O_5 + 14H_2O$. *Calcium vanadate*, $CaO,3V_2O_5 + 12H_2O$, is obtained in red, lustrous crystals by adding excess of ammonium vanadate to a solution of calcium nitrate containing a very small quantity of free nitric acid. It is very soluble in dilute acids; when heated, it loses water and forms a yellow powder. When calcium chloride is added in excess to ammonium vanadate no precipitate is formed, but on adding ammonia a bulky, white precipitate is produced, and when the liquid is boiled this changes to small, colourless, transparent needles grouped in nodules. It has the composition $2CaO,V_2O_5 + 2H_2O$, is very soluble in dilute acids, and loses water when heated, forming a yellow powder. *Nickel vanadate* separates in small, greenish-yellow, anhydrous prisms on boiling a mixture of ammonium vanadate with excess of nickel nitrate feebly acidified with nitric acid. It is very soluble in dilute nitric acid. If the brown-green mother-liquor is concentrated, it deposits greenish-brown, transparent crystals of the composition $NiO,2V_2O_5 + 3H_2O$. *Cobalt vanadate*, $CoV_2O_6 + 3H_2O$, is obtained in a similar manner; it is very soluble in water, and becomes anhydrous when heated.

Zinc vanadate, $ZnV_2O_6 + 2H_2O$, is also obtained in a similar manner in brilliant, pale-yellow, cubic or rhombic crystals which become anhydrous when heated. When a very dilute solution of copper

sulphate is mixed with ammonium vanadate, a precipitate is formed which dissolves on heating but becomes permanent if the copper sulphate is in excess. When boiled with the mother-liquor, it is converted into greenish-yellow, transparent, rhombohedral plates of *copper vanadate*, $3CuO,V_2O_5 + 3H_2O$. *Lead vanadate*, $2PbO,V_2O_5$, is obtained in sulphur-yellow, transparent, anhydrous prisms, terminated by pyramids, by boiling, in the mother-liquor, the precipitate which is formed when ammonium vanadate is added to a solution of lead nitrate acidified with acetic acid. *Silver vanadate*, $2Ag_2O,V_2O_5$, is obtained in brilliant golden-yellow, transparent, rhomboïdal plates, easily soluble in nitric acid, by dissolving in fused silver nitrate the precipitate produced by mixing solutions of silver nitrate and ammonium vanadate; the fused mass is cooled slowly and is then extracted with water. Silver vanadate dissolves in ammonia, and if the solution is evaporated over sulphuric acid it yields the compound $3AgVO_3,2(NH_4)_2O$ in brilliant, yellow, hexagonal needles grouped in mamelons. *Cadmium vanadate*, $CdO,3V_2O_5 + 2H_2O$, separates in small, brilliant red crystals on boiling the red liquid obtained by adding ammonium vanadate to a solution of cadmium nitrate acidified with acetic acid.

These crystalline metallic vanadates are analogous in constitution to the alkaline vanadates. C. H. B.

Ammoniacal Vanadates. By A. Ditte (*Compt. rend.*, **104**, 1844—1847).—*Methylamine Vanadates.*—The normal salt, $2MeNH_3VO_3 + H_2O$, is obtained in colourless, transparent needles by concentrating in a vacuum the strongly alkaline, straw-coloured liquid produced by mixing soluble vanadic anhydride with excess of methylamine. It is very soluble in water, and becomes brown when heated, then almost black, and, finally, takes fire and burns, leaving a residue of vanadic anhydride. The acid salt, $(NH_3Me)_2O,2V_2O_5 + 4H_2O$, is obtained in garnet-red rhomboïdal prisms on concentrating a solution of the normal salt acidified with acetic acid. It gives a yellow powder which becomes vermilion when heated, and finally takes fire and burns, leaving a residue of the anhydride.

Ethylamine treated in a similar manner yields a normal salt, NH_3EtVO_3, in the form of small, colourless, transparent, deliquescent crystals which on heating decompose with evolution of an inflammable gas, and leave a residue of vanadic anhydride. The acid salt, $(NH_3Et)_2O,2V_2O_5$, forms transparent, red prisms which burn like tinder when heated.

No magnesium ammonium vanadate could be obtained. Magnesium vanadate is decomposed by ammonia with formation of ammonium vanadate and magnesium hydroxide. Ammonium vanadate is only slightly soluble in concentrated ammoniacal solutions of magnesium hydroxide owing to the presence of ammonium chloride. In dilute solutions, no precipitate is formed, and when the liquid is concentrated ammonium vanadate and the double chloride, $MgCl_2,2NH_4Cl$, separate.

If a solution of ammonium vanadate, strongly acidified with acetic acid, is mixed with a cold dilute solution of potassium silicate, also acidified with acetic acid, and the red solution concentrated, the com-

pound $K_2O,2(NH_4)_2O,5V_2O_5 + 9H_2O$ is obtained in red transparent prisms. It may be regarded as a molecular compound of the two salts $K_2O,2V_2O_5$ and $2(NH_4)_2O,3V_2O_5 + 9H_2O$. When heated, it loses water, blackens, and gives off ammonia, yielding a residue which melts at a red heat. Sodium silicate yields a similar compound which crystallises with $15H_2O$ in brilliant, orange-red plates.

Vanadates, whether formed in the dry or wet way, correspond with a few well-defined and simple types, the most important of which are as follows:—

Acid Vanadates.—$M_2O,3V_2O_5$; $M_2O,2V_2O_5$; $2M_2O,3V_2O_5$.

Normal Vanadates.—M_2O,V_2O_5.

Basic Vanadates.—$2M_2O,V_2O_5$; $3M_2O,V_2O_5$; $4M_2O,V_2O_5$.

The proportion of water which these salts contain depends on the conditions of crystallisation. The more complex salts, $3M_2O,5V_2O_5$, may be regarded as compounds of a salt, $M_2O,2V_2O_5$, with a salt, $2M_2O,3V_2O_5$, like the double vanadates just described. C. H. B.

Metallurgy of Bismuth. By E. Matthey (*Proc. Roy. Soc.*, **42**, 89—94).—In order to separate gold and silver from bismuth, the author adds 2 per cent. of zinc to the molten metal, allows the mass to cool gradually, and removes the surface crust. This process is repeated. The whole of the gold and silver is found in the skimmings. The bismuth litharge so obtained is fused in a crucible with borax. The gold sinks to the bottom, being at the same time freed from any base metals by the action of the bismuth oxide. The slag is again fused with addition of bismuth to separate the last traces of gold.

The author separates bismuth from lead by means of repeated crystallisations, alloys of bismuth and lead melting at lower temperatures than bismuth itself. Bismuth holding 12 per cent. of lead contained only 0·4 per cent. after four crystallisations.

H. K. T.

Products of the Action of Acids on Alloys of the Platinum Metals. By H. Debray (*Compt. rend.*, **104**, 1667—1669).—The presence of a metal of the platinum group in solution in another metal such as tin, lead, or zinc, causes the latter to be much more readily attacked by dilute acids owing to the formation of innumerable minute galvanic couples. Under these conditions, the more oxidisable metal is dissolved by acids so dilute that they would have no action on it under ordinary circumstances. When the platinum metal combines with the other (*loc. cit.*), this compound forms galvanic couples with the excess of the oxidisable metal. In some cases (for example, the alloys of the platinum metals with tin) the alloy itself is attacked, especially if the acid is somewhat concentrated, and under these conditions some of the platinum metal is dissolved at the same time as the tin, &c.

When an alloy of zinc and osmium is treated with hydrochloric acid, or an alloy of lead with iridium or ruthenium is treated with nitric acid, the platinum metal is left undissolved in the form of minute crystals, since it is simply dissolved in the oxidisable metal. When combination has taken place between the metals, with development of heat, as in the case of lead and rhodium, the innumerable

galvanic currents which are developed when the regulus is treated with an acid give rise to the formation of a complex residue containing oxygen, nitrogen, and water in addition to rhodium and some lead. Unlike the alloys with tin, this particular alloy gives no definite compound when treated with an acid.

The formation of complex residues under the influence of galvanic currents which are due to the heterogeneity of metallic substances which are being dissolved in acids, is analogous to the formation of a silver peroxide or nitroxide when a solution of silver nitrate is electrolysed with silver electrodes. C. H. B.

Mineralogical Chemistry.

Graphite from Ceylon. By F. Sandberger (*Jahrb. f. Min.*, 1887, ii, Mem., 12—16).—The author has examined a large number of specimens of graphite from the gneiss of Ceylon. The specimens were in the form of irregular masses, 5 to 8 cm. in diameter, forming layers $1\frac{1}{2}$ to $2\frac{1}{2}$ cm. thick round other minerals. In some cases, crystals were developed, the planes observed being $\infty P\infty$, P, $\frac{1}{2}P\infty$. In many places on the principal cleavage plane ($\infty P\infty$), needles were observed crossing one another at angles of 60° and 120°. These needles are mostly colourless, sometimes black. They resemble those in the mica of Ontario, and in the biotite from the mica diorite of Vöhrenbach. The colourless needles consist of rutile, whilst the few dark ferriferous needles appear to be pseudomorphs of titaniferous iron ore after rutile. Colourless massive quartz with conchoidal fracture is the most frequent of the minerals which are surrounded by the graphite. Granular quartz is of rarer occurrence. In two specimens, the centre consisted of green orthoclase. In another case, the centre consisted of olive-green apatite; whilst in other cases the centre consisted of kaolin, formed from the alteration of triclinic felspar. (Compare Abstr., 1886, 774.) B. H. B.

Recent Formation of Marcasite at Marienbad. By E. Palla (*Jahrb. f. Min.*, 1887, ii, Mem., 5—7).—Hollow tubes of pyrites are found in the peat bog of Marienbad. They are casts of plant remains, and are found to be composed of marcasite. Their sp. gr. is 4·46. Analysis of the bog water gave the following percentages:—

Fe_2O_3.	SO_3.	CaO.	MgO.
0·02	0·11	0·04	0·01

The water of the bog containing the pyrites-mass is thus remarkable for the percentage of ferrous sulphate and of gypsum. The recent formation of the pyrites appears to be due to the reduction process brought about by the presence of plants in the ferrous sulphate.

B. H. B.

Percylite, Caracolite, and Phosgenite from Chili. By F. Sandberger (*Jahrb. f. Min.*, 1887, ii, Mem., 75—77).—A specimen of galena in a dark quartzose gangue, from the Sierra Gorda in Chili, is covered with yellow, blue, colourless, and white crusts of substances of more recent formation. Careful examination shows that these crusts occur in regular order, the blue substance being older than the colourless, and the colourless older than the white. The blue substance is lead-copper oxychloride, or percylite. The colourless substance is caracolite. The white mineral occurring above this appears to be a new compound of phosgenite ($PbCO_3,PbCl_2$) with sodium sulphate. All these minerals are undoubtedly products of the action of a salt solution on a mineral vein containing bournonite and galena. B. H. B.

Minerals from the Sjö Mine, Sweden. By L. J. Igelström (*Jahrb. f. Min.*, 1887, ii, Mem., 8—11).—The Sjö mine, in the parish of Grythyttan, Oerebro, Sweden, is a small mine only a few fathoms in depth. Exploratory workings, however, have shown that the ore deposit extends for a considerable length. The mine is a very ancient one, and, after having been abandoned for centuries, it was re-opened in 1885. The ore bed has a thickness of 5 metres, and the ore, braunite and hausmannite, is very rich and pure. Adjoining this manganese ore bed is a bed of iron ore, hæmatite, and magnetite of poor quality. Both ore beds are enclosed in dolomite, which forms a bed in the granulite nearly a mile in length, and several hundred yards in width. The braunite and hausmannite of the Sjö mine are accompanied by a large number of remarkable minerals, such as xanthoarsenite (Abstr., 1886, 25), hæmatostibiite, polyarsenite, and pyrrhoarsenite. The minerals usually met with in this mine are the following:—Tephroite, iron glance, magnetite, calcite, garnet, rhodonite, specular iron ore. Barytes, chlorite, neotocite, and galena are of rare occurrence.

Pyrrhoarsenite, a mineral discovered by the author in July, 1886, is an anhydrous arsenate of manganese, calcium, and magnesium, containing 17 per cent. of manganous oxide. B. H. B.

Mineralogical Notes. By V. v. Zepharovich (*Jahrb. f. Min.*, 1887, ii, Ref., 21).—1. *Pyroxene from the Krimlerthal.*—On the crystals, the predominating planes are $\infty P\infty$, $\infty P\infty$, $P\infty$, ∞P. The plane $-P$ is very small, and the planes $\infty P3$, $\infty P3$, $2P\infty$, $+P$, $+2P$, are of rare occurrence. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.
52·08	1·36	2·56	8·93	0·49	10·60	21·59	2·06

The angle made by the direction of extinction with the vertical axis on cleavage plates parallel to $\infty P\infty$ is 46° 40′.

2. *Scheelite from the Krimlerthal.*—The crystals exhibit the planes $\frac{1}{2}P\infty$, $P\infty$, 3P3, P, P3, 2P2, the last being new for this mineral.

B. H. B.

Dipyr from Connecticut. By A. Arzruni (*Jahrb. f. Min.*, 1887, ii, Ref., 9—10).—The author describes some crystals of dipyr from Canaan, Connecticut, presented to the University of Breslau by A. D. Roe. The crystals average 2 cm. long and 1 cm. thick. They are sometimes colourless and transparent, sometimes grey. The crystals-forms observed are $\infty P\infty$, ∞P, P. The edges and angles are rounded. The axial ratio is $a : c = 1 : 0{\cdot}4401$, being that of meionite. The mineral exhibits a faint basal cleavage. There is no distinct prismatic cleavage as is usually stated in works on mineralogy.

B. H. B.

Heulandite. By P. Jannasch (*Jahrb f. Min.*, 1887, ii, Mem., 39—44).—The author gives the results of analyses of heulandite (I and II) from St. Andreasberg and (III) from the Fassathal.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	SrO.	MgO.	K_2O.	Na_2O.
I.	56·11	17·07	trace	4·25	3·62	trace	0·36	3·49
II.	56·10	17·24	trace	4·27	3·65	trace	0·18	3·14
III.	60·07	14·75	0·62	4·89	1·60	—	0·44	2·36

	Li_2O.	H_2O.	Total.	Sp. gr.
I.	trace	16·19	101·09	2·247
II.	trace	16·37	100·95	—
III.	trace	15·89	100·62	2·196

All the varieties of heulandite analysed by the author contain strontium. (Compare Abstr., 1887, 453.) B. H. B.

Mineralogical Notes. By H. Traube (*Jahrb. f. Min.*, 1887, ii, Mem., 64—70).—1. *Laubanite, a new Zeolite.*—The author has analysed a specimen of a zeolite supposed to be desmine occurring with phillipsite on an unaltered basalt from Lauban in Silesia. The hardness of this mineral was greater than that of desmine, and the mineral exhibited no lustre. Analysis showed that this mineral is a new zeolite having the composition $Al_2Ca_2Si_5H_{12}O_{21}$. The name of *laubanite* is proposed for it after the locality where it is found. Analysis gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
47·84	16·74	0·56	16·17	1·35	17·08	99·74*	2·23

In chemical composition laubanite approaches nearest to laumontite: whilst it differs from phillipsite in the absence of sodium silicate, as well as in its proportion of water. Laubanite is snow-white in colour. It is transparent only in thin sections, and has no lustre. Its hardness is 4·5 to 5. It forms small monoclinic crystals, 3 to 5 mm. in size.

2. *Laumontite and Scolezite from Striegau.*—Colourless crystals of laumontite are frequently found at Striegau on orthoclase and quartz, associated with desmine, epidote, and axinite. Externally, this mineral cannot be distinguished from fibrous snow-white scolezite. The latter occurs at the same locality in association with heulandite, but never

* 99·76 in original.

in crystals on orthoclase. Analyses of the two minerals gave the following results: I, laumontite, II, scolezite :—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	51·09	21·36	11·76	—	15·35	99·56	2·28
II.	46·48	25·53	13·38	0·68	13·69	99·76	2·31

B. H. B.

Trachytic Rocks from the Island of San Pietro. By F. Eigel (*Jahrb. f. Min.*, 1887, ii; Ref., 92—93).—San Pietro, an island on the south-west coast of Sardinia, is composed principally of recent eruptive rocks. Analyses are given of (I) red liparite from Spalmatore, consisting of a dense fibrous ground-mass with sphærolites of chalcedony and disseminated sanidine and biotite, (II) black obsidian with sanidine and augite, and sphærolites of quartz.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	76·84	5·87	3·92	0·87	0·73	3·34	0·52
II.	70·03	18·63	0·11	—	—	2·62	0·10

	Na_2O,K_2O.	H_2O.	Total.	
I.	5·41	1·69	99·19	
II.	3·15	4·28	98·92	B. H. B.

The so-called Trachyte-dolerites of the Vogelsberg. By J. M. Ledroit (*Jahrb. f. Min.*, 1887, ii; Ref., 81—82).—According to Tasche and Ludwig, the trachyte-dolerites of the Vogelsberg are rocks intermediate between trachyte and dolerite, containing oligoclase, labradorite, hornblende, augite, and magnetite. The author considers the name of trachyte-dolerite unsuitable for these rocks, and distinguishes two varieties, dolerite and plagioclase-basalt. The latter has a sp. gr. of 2·884, and is composed of olivine, plagioclase, augite, magnetite, apatite, and a colourless glass. Analyses are given of a trachyte-dolerite from Laubach (I), of a basalt from Michelneu (II), and of a basalt, very rich in augite, from Gedern (III).

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.
I.	48·39	13·29	8·23	7·81	8·81	8·48	0·90	2·67
II.	47·38	12·51	12·47	7·13	8·83	6·24	0·73	3·80
III.	41·32	12·27	15·13	7·36	10·33	3·56	0·84	4·19

	H_2O.	CO_2.	P_2O_5.	TiO_2.	Loss on ignition.	
I.	1·81	0·36	0·97	0·25	1·86	
II.	2·79	0·18	0·97	—	2·34	
III.	4·38	0·20	0·97	0·35	3·97	

B. H. B.

The Pallasite from Campo de Pucará. By E. Cohen (*Jahrb. f. Min.*, 1887, ii, Mem., 45—52).—The author has received a fragment, weighing 37 grams, of the pallasite found in 1879 at Campo de Pucará, in the State of Catamarca, in the Argentine Republic. From its remarkable resemblance to the pallasite of Imilac, Atacama, the author was induced to submit this meteorite to a careful investigation.

He found that the similarity of the two pallasites extends to their microscopic structure and chemical composition.

Two analyses of the metallic portion of the Campo de Pucará pallasite gave the following results (I and II) :—

	Residue.	Fe.	Ni.	Co.	Cu.	Total.
I.	0·09	90·81	9·02	0·53	trace	100·45
II.	1·11	89·72	8·67	0·57	trace	100·07
III.	—	88·01	10·25	0·70	—	—

For comparison, Frapolli's analysis of the Imilac pallasite (III) is added. The remaining 1·04 per cent. consists of magnesium, calcium, sodium, potassium, and phosphorus. B. H. B.

Organic Chemistry.

Substitution-derivatives of Methylene Chloride. By R. Höland (*Annalen*, **240**, 225—243).—Alcoholic ammonia and methylene chloride heated together at 125° yield hexamethylenamine and ammonium chloride. Chlorine, both free and as phosphoric chloride, decomposes methylene iodide, yielding methylene chloride and traces of chloroform. With methylene bromide, the same reagents at 190° yield carbon tetrachloride and carbon tetrabromide, iodine chloride and iodine trichloride; with methylene chloride at 220° both yield chloroform and perchlorobenzene; iodine bromide and methylene chloride at 200° yield iodoform and small quantities of *iodomethylene chloride*, $CHICl_2$, and *diiodomethylene chloride*, CI_2Cl_2. The former is a colourless oil, boils at 131°, and has an irritating odour. The latter crystallises in small scales, melts at 85°, and boils with decomposition at 185°. Iodine tribromide and methylene chloride at 180° yield bromoform, carbon tetrabromide, and perbromethylene, C_2Br_4. The author finds that the latter compound is also formed by heating CBr_4 at 220°. Potassium iodide and iodine when heated with methylene chloride in alcoholic solution at 200° yield ether, ethyl iodide, and methylene iodide; without alcohol no reaction takes place at 210°. Phosphoric pentiodide has no appreciable action on methylene chloride at 210°; free iodine at the same temperature yields methylene iodide.

When pure dry sodium glycerate, $NaC_3H_7O_3$, is heated with methylene chloride at 100° for two hours, diglycerylmethylal (methylene diglyceryl oxide) $CH_2(O{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2OH)_2$ is formed. This is an almost colourless syrup, soluble in alcohol and ether, insoluble in water. It decomposes on distillation. L. T. T.

Preparation of Allyl Iodide and Allyl Alcohol. By A. Béhal (*Bull. Soc. Chim.*, **47**, 875—877).—Allyl iodide may be conveniently prepared by the following modification of Berthelot and de Luca's

method (*Ann. Phys. Chim.* [3], **43**, 257). 2000 grams of commercial glycerol, 60 grams of iodine, and 200 grams of red phosphorus are introduced into a tubulated retort and the whole well mixed. The retort is connected with a condenser and heated until frothing occurs, when the heat is regulated so that a gentle ebullition is maintained, and a solution of 440 grams of iodine in 160 grams of allyl alcohol is added drop by drop. The distillate of allyl iodide in the receiver is slightly coloured by iodine, and at the end of the operation is returned to the retort and redistilled, when it is obtained quite colourless. The whole operation lasts about five hours and a half. After its completion, the residue in the retort is further heated, and an aqueous distillate containing a small quantity of allyl iodide and a considerable amount of allyl alcohol (about 100 grams from the above quantities) is obtained; a certain amount of a viscous liquid, which appears to be a mixture of di- and tri-glycerol, is also formed. The yield of allyl iodide is about 637 grams, the theoretical yield being 661 grams. The advantages which the author claims for this process are that a large quantity of allyl iodide may be prepared at a time without any danger of an explosion; that only the merest traces of isopropyl iodide are formed; and that allyl alcohol is obtained as a valuable bye-product. A. P.

Sulphuranes. By R. Demuth and V. Meyer (*Ber.*, **20**, 1830—1831).—The authors give the name *sulphuranes* to the class of bisulphides, several members of which have been described by Mansfield (this vol., p. 122) and by V. Meyer (this vol., p. 228). The authors have proved the correctness of the general formula $C_2H_3{\cdot}S{\cdot}C_2H_4{\cdot}SR$, by obtaining the ethyl vinyl ether of ethylene mercaptan, and proving it to be identical with ethylsulphurane. The compound $OH{\cdot}C_2H_4{\cdot}SEt$ was obtained by acting on ethyl hydrosulphide with ethylene chlorhydrin. This was treated with phosphoric chloride and converted into $Cl{\cdot}C_2H_4{\cdot}SEt$, which with potassium hydrosulphide yielded $SH{\cdot}C_2H_4{\cdot}SEt$. The sodium salt of the latter when treated with ethylene chlorhydrin gave $OH{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}SEt$, which when acted on by phosphoric chloride yielded $Cl{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}SEt$; the latter when heated with alcoholic potash forms $C_2H_3{\cdot}S{\cdot}C_2H_4{\cdot}SEt$, which is identical with the ethylsulphurane obtained from diethylene disulphide ethiodide. L. T. T.

Isodulcitol. By J. Herzig (*Monatsh. Chem.*, **8**, 227—229).—The author confirms Fischer's and Will's description of the phenylhydrazine compound of this sugar (Abstr., this vol., pp. 652 and 715). When oxidised with silver oxide, isodulcitol is completely split up into acetic acid. Chromic acid gives the same result. G. H. M.

Isodulcitol. By B. Rayman (*Bull. Soc. Chim.*, **47**, 668—677, and 760—761).—Isodulcitol melts at about 90·9°, when heated at 100° to 105° for seven hours it loses a molecule of water, and at 130° it becomes brown and decomposes. Its rotatory power $[\alpha]_D = +8{\cdot}61°$. It reduces Fehling's solution, the reducing power varying with the concentration; it immediately reduces ammoniacal silver solution,

forming a mirror. Knapp's reagent is also reduced. When added to an alkaline solution of picric acid, picramic acid is formed. It decolorises alkaline solutions of indigo or potassium ferricyanide; but gives no reaction with a bleached solution of rosaniline.

When isodulcitol is treated with iodine and potash, a mere trace of iodoform is obtained. With α-naphthol and concentrated sulphuric acid, it yields a bluish-violet coloration, and on the addition of water a dirty-green precipitate is thrown down; with thymol, it forms a crimson ring which rapidly becomes brown; with resorcinol, it yields a red coloration, a precipitate being formed on the addition of water. On mixing concentrated solutions of phenylhydrazine and isodulcitol, the compound $C_{12}H_{18}N_2O_4$ is gradually formed; it is very sparingly soluble in alcohol. When phenylhydrazine hydrochloride, sodium acetate, and isodulcitol are heated in aqueous solution, the compound $C_{18}H_{22}N_4O_3$ is produced; it crystallises from water, is of a yellow colour, melts at 171°, and seems to be identical with the compound described by Fischer and Tafel (this vol., p. 651).

On agitating 5 grams of isodulcitol dissolved in 230 c.c. of a 10 per cent. aqueous solution of sodium hydroxide with 30 grams of benzoyl chloride, an oily substance separates, which on cooling solidifies and may be recrystallised from alcohol; it consists of a mixture of *tribenzoylisodulcitol*, $C_6H_{11}(C_7H_5O)_3O_6$, and *tetrabenzoylisodulcitol*, $C_6H_{10}(C_7H_5O)_4O_6$. Glacial acetic acid does not seem to have any action on isodulcitol, but 4 parts of acetic anhydride heated at 120° with 1 part of isodulcitol yields *isodulcitol monacetate*, $C_6H_{11}O_5,C_2H_3O$, which is obtained as a resin resembling monosuccinin. By heating 1 part of isodulcitol with 5 parts of acetic anhydride at 140°, a mixture of *isodulcitol diacetate* and *triacetate* was obtained in the form of a resinous mass. By heating 1 part of isodulcitol with 10 parts of acetic anhydride and 1 part of sodium acetate for eight hours at 140°, a resinous *isodulcitol tetracetate*, $C_6H_8(C_2H_3O)_4O_5$, is obtained.

Isodulcitol dissolves in sulphuric acid without alteration, but nitric acid oxidises it energetically; on treating isodulcitol with a mixture of nitric and sulphuric acids a very unstable *isodulcityl trinitrate*, $C_6H_9(NO_2)_3O_6$, is formed; it is decomposed by water. On heating isodulcitol with dilute hydrochloric acid, humous substances, formic acid, and a non-volatile acid which reduces silver salts are formed. Hydriodic acid and phosphorus have no action on isodulcitol.

From the above results, the author concludes that isodulcitol and arabinose are aldehydes whose corresponding penthydric alcohols are not yet known, but may probably be obtained by the reduction of these two compounds; he further proposes to divide the sugars into the following three classes:—

I. Tetravalent alcohol: erythrol.

II. Pentavalent alcohols: 1. (*a*) Normal, at present unknown, but possibly may be obtained by the reduction of isodulcitol and arabinose; (*b*) having a closed ring nucleus: quercitol. 2. The corresponding aldehydes and acetones: arabinose and isodulcitol.

III. Hexavalent alcohols: 1. (*a*) Normal: the physical isomerides mannitol, dulcitol, and perseïte; (*b*) having a closed ring nucleus: inosite. 2. The corresponding aldehydes: dextrose and galactose.

3. The corresponding acetone: lævulose. 4. Products of the condensation of the aldehydes: as saccharones, &c. A. P.

Derivatives of Inosite. By MAQUENNE (*Compt. rend.*, **104**, 1719—1722).—*Inosite hexacetin*, $C_6H_6(C_2H_3O_2)_6$, is obtained by heating inosite with acetic chloride or acetic anhydride at 120—170°, or by boiling anhydrous inosite and acetic anhydride with fused zinc chloride. When the product is treated with water, the acetin is left as a crystalline powder insoluble in water, but soluble in hot alcohol or hot acetic anhydride. It begins to sublime at 200°, melts at 212°, and boils without decomposition at 234° in a vacuum. In presence of air, it rapidly becomes brown when heated, even under reduced pressure. Alcoholic alkalis decompose it rapidly with reproduction of inosite.

The hexacetin is obtained mixed with an amorphous product which is soluble in water and alcohol; this is decomposed by alkalis with production of inosite which yields a crystalline acetin when treated as above. It is probably a mixture of non-saturated acetins.

Inosite hexabenzoïn, $C_6H_6(C_7H_5O_2)_6$, is obtained by the action of benzoic chloride on inosite. The product is treated with water, and then boiled with alcohol, which dissolves out a mixture of intermediate products, and leaves the benzoic derivative in crystals which are insoluble in all ordinary solvents. It melts at 258°, and is readily decomposed by alkalis.

. *Inosite hexanitrin* was prepared by Vohl's method (*Annalen*, **101**, 55), and is very unstable, detonating violently when struck. With warm alcoholic potash, it yields potassium nitrite and a yellow amorphous substance which is a product of the oxidation of inosite, and is similar in appearance to the products of the decomposition of the hydroxyquinones. If an alcoholic solution of the nitrin is mixed with potash and saturated with sulphurous anhydride, it yields a copious crystalline precipitate of potassium nitrilosulphite, $N(SO_3K)_3 + 2H_2O$. When the nitrin is boiled with ethyl alcohol mixed with sulphuric acid, it yields inosite and ethyl nitrite. These reactions show that it is a true ethereal salt, and not a nitro-phenol.

Tetrabenzoylquinone, $C_6O_2(C_7H_5O_2)_4$, is easily obtained by boiling tetrahydroxyquinone for a few minutes with benzoic chloride. It crystallises in beautiful yellow needles, and its formation proves that tetrahydroxyquinone contains four OH groups, and has the constitution ascribed to it by Nietzki and Benckiser (*Ber.*, **18**, 499). Acetic chloride yields a similar derivative, which however is very difficult to purify.

Haloïd ethers of inosite could not be obtained. Hydrochloric acid has no action even at 200°. Phosphorus trichloride and phosphorus pentabromide attack the inosite at a high temperature, with carbonisation. Phosphorus pentachloride at 150° produces hydrogen chloride and phosphorus acid, together with a white, viscous, unstable product. If inosite hexachlorhydrin exists at all, it must be much less stable than benzene hexachloride. If the latter compound is heated with silver acetate and acetic anhydride at 170° for 30 hours, it yields no trace of inosite hexacetin.

Inosite is a hexahydric alcohol derived from hexamethylene. It must be regarded as a mannitol with a closed chain, and not as a polyhydric phenol. C. H. B.

Identity of Dambose with Inosite. By Maquenne (*Compt. rend.*, **104**, 1853—1855).—Dambose obtained by the action of hydriodic acid on dambonite prepared from caoutchouc (Girard, *Compt. rend.*, **67**, 820; **73**, 426; **76**, 995) is identical with inosite in composition, crystalline form, melting point, and all other properties. The hexacetins obtained from the two compounds are likewise identical. C. H. B.

Carbohydrate from Acorns. By C. Vincent and Delachanal (*Compt. rend.*, **104**, 1855—1858).—In the preparation of quercitol by Prunier's method (*Ann. Chim. Phys.* [5], **15**, 5), if the syrupy liquid which will not crystallise is mixed with dilute sulphuric acid in sufficient quantity to convert the potassium and calcium into sulphates, evaporated in a vacuum on a water-bath until a white saline deposit is formed, and then mixed with an equal volume of alcohol, practically the whole of the calcium and potassium is precipitated, and if the filtered liquid is further concentrated in a vacuum it yields an additional quantity of crystallised quercitol.

During this last crystallisation, crystals separate which differ from quercitol in form, and effloresce rapidly in air or in a vacuum. This substance can be recrystallised from water at a low temperature, and forms bulky, transparent, hexagonal prisms which rapidly become opaque by efflorescence. In a closed tube, the crystals remain transparent at 30°, but give off water, and when examined under a microscope are found to have become converted into small, anhydrous, monoclinic prisms. The effloresced crystals have the same form. This compound has the composition $C_6H_{12}O_6$. It is soluble in warm water, from which it separates in anhydrous prisms, the hydrated crystals only being formed at low temperatures. It is comparatively insoluble in cold water, and is insoluble in boiling alcohol. It melts at 340° without decomposition, but at a higher temperature decomposes and emits an odour of burnt sugar. Its solutions are optically inactive.

When treated with acetic anhydride, this compound yields an acetin, $C_6H_6(C_2H_3O_2)_6$, crystallising in long, rhombic prisms which melt at 301°, are readily volatile, and are insoluble in water and ether, but can be recrystallised from boiling alcohol. The formation of this derivative indicates that the original compound has the constitution $C_6H_6(OH)_6$. It does not ferment with yeast, and does not reduce Fehling's solution even after being boiled with a dilute acid. It gives no coloration with boiling soda solution, and forms no compound with phenylhydrazine in warm acetic acid. It reduces ammonio-silver nitrate after addition of soda. When evaporated with nitric acid on platinum-foil, treated with ammoniacal calcium chloride, and again evaporated, it yields a red coloration similar to that produced by inosite, so that this reaction is not characteristic of inosite.

This compound, for which the authors propose the name *quercin*, is

isomeric but not identical with inosite, from which it differs in crystalline form, melting point, and solubility, and in the melting point of its hexacetin. C. H. B.

Polyiodides. By A. Geuther (*Annalen*, **240**, 66—85).—The tri- and penta-iodides were prepared by dissolving the simple iodide and the necessary amount of iodine in warm alcohol.

Tetramethylammonium enneaiodide, NMe_4I_9, crystallises in thin plates melting at 110°.

Tetrethylammonium heptiodide, NEt_4I_7, is obtained crystallising in dark-violet plates which melt at 108°.

Phenyltrimethylammonium triiodide forms brown plates melting at 115°. The penta-iodide crystallises in green needles with a metallic lustre; it melts at 82°. The *heptiodide* melts at 65°.

Phenyldimethylethylammonium triiodide, $NPhMe_2EtI_3$, is dark violet, and melts at 81°. The *penta-iodide*, $NPhMe_2EtI_5$, forms dark bluish-green plates with a metallic lustre which melt at 50°. The *heptiodide* crystallises in dark bluish-violet plates which melt at 45°.

Trimethylethylammonium pentiodide melts at 26° (not 68°; Müller, *Annalen*, **108**, 1).

Trimethylethylammonium enneaiodide, NMe_3EtI_9, is dark green, and melts at 38°.

Triethylmethylammonium pentiodide, NEt_3MeI_5, crystallises in dark-green plates melting at 16°. The *heptiodide*, NEt_3MeI_7, forms dark brown-violet plates melting at 42°.

Tables are given containing the formulæ, melting points, colour, and crystalline form of the polyiodides. The tri- and penta-iodides are reddish-brown or violet-blue, the hepta- and ennea-iodides green. The constitution of the polyiodides, and the number of atoms contained in the mols. of crystallised, liquid, and gaseous iodine respectively is discussed. N. H. M.

Crystallographic Examination of some Polyiodides. By O. Lüdecke (*Annalen*, **240**, 85—92).—Tetramethylammonium enneaiodide forms tabular crystals, probably rhombic.

Tetrethylammonium heptiodide forms dark-brown rhombic crystals.

Phenyltrimethylammonium triiodide crystallises in brown rhombic plates.

Phenyltrimethylammonium pentiodide forms monoclinic crystals; $a : b : c = 1{\cdot}7943 : 1 : 1{\cdot}2511$; $\beta = 69° 43'$.

Phenyltrimethylammonium heptiodide crystallises in plates, probably monoclinic.

Phenyldimethylethylammonium triiodide forms rhombohedric crystals.

Phenyldimethylethylammonium pentiodide forms dark-green plates.

Trimethylethylammonium pentiodide crystallises in plates which seem to be rhombic.

Trimethylethylammonium triiodide forms regular crystals. (Compare Müller, *Annalen*, **108**, 1.) N. H. M.

Action of Hydroxylamine on Acetamide. By C. Hoffmann (*Ber.*, 2204—2205).—Ethenylamidoxime is formed when aqueous solutions of acetamide and hydroxylamine are mixed and left for some time at the ordinary temperature, the reaction even occurring if hydroxylamine hydrochloride is substituted for the free base.

A. J. G.

Glyoxal-œnanthyline and its Derivatives. By M. Karcz (*Monatsh. Chem.*, **8**, 218—223).—Glyoxal-œnanthyline was prepared by Radziszewski's method (Abstr., 1883, 1086). It is a snow-white substance consisting of microscopic crystals, it melts at 50—51°, and boils at 294—296°. It is easily soluble in alcohol, ether, and benzol, insoluble in water. It differs in melting point from the substance described by Radziszewski (*loc. cit.*); this the author ascribes to the fact that the substance exists in two allotropic forms. The *hydrochloride* and *hydrobromide* crystallise in long, thin, colourless needles, which instantly deliquesce in the air; the *oxalate* forms snow-white crystals melting at 121°. The *platinochloride* forms yellow needles, easily soluble in water, alcohol, and ether; the *platinobromide* is a purple-red crystalline powder, also soluble in water, alcohol, and ether.

Oxalmethyl-œnanthyline, $C_9H_{15}MeN_2$, is obtained by digesting a solution of glyoxal-œnanthyline in methylic alcohol with methylic iodide in a reflux apparatus, and after distillation of the methylic alcohol treating the residue with potash. It is a colourless, oily liquid of unpleasant smell, boils at 261—263°; sp. gr. at 16·5°, 0·9282; it is insoluble in water, soluble in alcohol and ether. It gives all the reactions of an alkaloïd. The *platinochloride* crystallises in bright yellow plates with a golden lustre, and is soluble in water, alcohol, and ether.

Oxalethyl-œnanthyline, $C_9H_{15}(Et)N_2$, is prepared in the same way from glyoxal-œnanthyline and ethylic bromide. It is a colourless oily liquid, its sp. gr. at 16·5° is 0·9210, and it boils at 270—272°. The *platinochloride* resembles the corresponding salt of oxalmethyl-œnanthyline.

Oxalpropyl-œnanthyline, $C_9H_{15}(Pr)N_2$, is obtained in a manner similar to the above; it is a colourless oily liquid boiling at 285—286°; its sp. gr. at 17° is 0·9192. The *platinochloride* crystallises in yellow, lustrous plates, is easily soluble in alcohol and ether, less readily in water.

The above oxalines behave in all respects exactly like those described by Radziszewski.

G. H. M.

Triethyl Formate and various Methylals. By M. Arnhold (*Annalen*, **240**, 192—208).—The author has examined the action of reagents on triethyl formate, $CH(OEt)_3$, in the hope of obtaining derivatives which might help to determine the equality or non-equality of the various carbonyl-affinities. He finds, however, that this salt is too unstable to allow of the formation of such intermediate or mixed derivatives. Phosphoric and phosphorous chlorides, bromine, iodine, nitric acid and nitrous anhydride cause decomposi-

tion of the compound. Hydrochloric acid yields monethyl formate and ethyl chloride.

The author has prepared a number of methylene ethers (methylals), $CH(OR)_2$, by the action of the corresponding sodium alcoholates on methylene chloride. The lower homologues are colourless mobile liquids of pleasant odour, the higher homologues thick oily liquids or solids, often pale-yellow in colour and of unpleasant odour. The following table gives their chief characteristics.

	M. p.	B. p. (corr.).	Sp. gr.	
Methylene dimethyloxide...	—	41·5°	0·854 at 20°	Mobile liquid.
„ diethoxide.....	—	87·0	0·834 „	„ „
„ dipropyl oxide..	—	137·2	0·8345 „	Thick liquid.
„ diisopropyl oxide	—	118·5	0·831 „	Oily liquid.
„ diisobutyl oxide .	—	164·3	0·825 „	„ „
„ diisoamyl oxide..	—	207·3	0·835 „	„ „
„ dioctyl oxide....	—	above 360°	0·846 „	Thick oily liquid.
„ diphenyl oxide ..	—	298·8°	1·092 „	„ „
„ dibenzyl oxide ..	—	above 360°	1·053 „	„ „
„ diorthocresyl oxide.....	32·5°	—	1·019 at 50°	Crystalline solid.
„ diparacresyl oxide.....	40·2	above 360°	1·034 „	„ „
„ dimetacresyl oxide.....	45°	„ „	1·052 „	„ „
„ dithymyl oxide..	36	„ „	0·979 „	„ „

In the hope of obtaining acid derivatives of methylene, methylene chloride, sodium acetate, and alcohol were heated together at 170°. Methylene diethoxide, ethyl acetate, sodium chloride, and acetic acid were formed. No reaction took place when dry sodium acetate and methylene chloride were heated together, even at 260°.

By the action of bromine on methylene chloride, $CHBrCl_2$ and CBr_2Cl_2 were formed. The latter is colourless, melts at 38° and boils at 150·2°. L. T. T.

Preparation of Ethyl α-Bromopropionate. By N. Zelinsky (*Ber.*, **20**, 20—26).—400 grams of bromine is added by drops to 300 grams of propionic acid in presence of 31 grams of amorphous phosphorus, and the whole left until no more hydrogen bromide is evolved. It is then heated on a water-bath and gradually treated with 640 grams of bromine. When no more bromine-vapour is visible in the condenser the product is allowed to become cool, treated with absolute alcohol, the ethyl salt precipitated with water, washed and fractionally distilled. The yield of ethyl α-bromopropionate is 640 grams. N. H. M.

β-Dichloropropionic Acid. By G. Fromme and R. Otto (*Annalen*, **239**, 257—272).—β-Monochloracrylic acid, prepared by Wallach's process from chloralide, is converted into β-dichloro-

propionic acid by the action of hydrochloric acid (40 per cent.) in sealed tubes at 80°.

Dichloropropionic acid crystallises in colourless prisms and melts at 56°. The acid dissolves freely in alcohol, ether, chloroform, benzene, and water. The *ethylic* salt, $C_2H_3Cl_2{\cdot}COOEt$, is a colourless liquid, possessing a fruit-like odour. It is slightly heavier than water and boils between 171° and 175°. When saponified with alcoholic potash, it yields β-monochloracrylic acid, showing that the dichloropropionic acid is really the β-compound. The *amide*, $C_2H_3Cl_2{\cdot}CONH_2$, crystallises in white needles or plates. It melts at 140°, and is soluble in water and alcohol, forming fluorescent solutions. W. C. W.

Acids from Drying Oil. By K. Hazura (*Monatsh. Chem.*, **8**, 260—270. Compare this vol., pp. 359, 798).—Peters (this vol., p. 126, Dieff and Reformatzky (this vol., p. 716), and the author (this vol., p. 359) have on different grounds concluded that the formula of linoleic acid is $C_{18}H_{32}O_2$ and not $C_{16}H_{28}O_2$. In order to set this point at rest, the author has undertaken the present research. When sativic acid (Abstr., 1886, 868) is oxidised with alkaline potassium permanganate, the only solid product obtained is azelaic acid.

When linoleic acid is treated with bromine, the hexabromo-compound, $C_{18}H_{30}Br_6O_2$, is the only product. When the tetrabromo-derivative of the acid from hemp oil is treated with excess of bromine, no further bromination takes place, showing that the above-mentioned hexabromo-compound is not derived from this.

The linoleic acid from linseed oil gave an "iodide value" which corresponds with a mixture of two acids, one with the formula $C_{18}H_{32}O_2$, the other with the formula $C_{18}H_{30}O_2$. The formation of a tetra- and hexa-bromo-derivative and of linusic acid and sativic acid on oxidation also support the view that linoleic acid is a mixture. The author prepared the $C_{18}H_{32}O_2$ acid from the tetrabromo-compound and the $C_{18}H_{30}O_2$ from the hexabromo-derivative; for the former, he proposes the name *linolic acid*, for the latter *linolenic acid*.

If *linolic acid*, prepared from the tetrabromo-derivative, is oxidised with alkaline potassium permanganate, it yields sativic and azelaic acids, but no linusic acid; when treated with bromine, it gives *tetrabromolinolic acid*, melting at 114—115°.

Linolenic acid, $C_{18}H_{30}O_2$, prepared from the hexabromo-compound melting at 177°, has an "iodine value" of 245, and yields on oxidation no solid acid but linusic acid (m. p. 201°). With bromine, nothing but the *hexabromolinolenic acid* is formed.

These experiments clearly show that the acids from drying oils contain both linolic acid, $C_{18}H_{32}O_2$, and linolenic acid, $C_{18}H_{30}O_2$. The author proposes to examine the acids from poppy oil, hemp-seed oil, and nut oil, which give only sativic acid on oxidation. He enunciates the following law for the oxidation of the unsaturated fatty acids: these acids when oxidised in alkaline solution with potassium permanganate add as many (OH)-groups as they contain free valencies, and form saturated acids which contain the same number of carbon-atoms in the molecule. On this law, he founds an exact qualitative method for the examination of fats and oils. G. H. M.

Turkey-red Oil. By R. Benedikt and F. Ulzer (*Monatsh. Chem.*, 8, 208—217).—The authors review previous work on this subject (see Abstr., 1884, 946; 1885, 313 and 315) and have prepared the sulpho-acid of a higher fatty acid in order to compare its behaviour with that of the Turkey-red oil soluble in water.

Sulpholeic acid was prepared by heating pure oleic acid (10 parts) at 200—220° with sulphur (1 part). Sulphuretted hydrogen is copiously evolved, and the sulphur is completely dissolved. The sulpho-acid was separated from the unaltered oleic acid by means of the barium salt. When sulpholeic acid is oxidised with potassium permanganate in alkaline solution, it yields a sulpho-fatty acid—*sulphohydroxystearic acid;* this substance and the soluble fatty acid of Turkey-red oil from olive oil behave in many respects in the same manner. Both are miscible with water in all proportions, and are precipitated by sodium chloride and dilute acids; neither are decomposed when boiled for some hours with aqueous potash. In other respects the two acids differ in behaviour, and the author concludes that the Turkey-red oil is the acid sulphate of hydroxystearic acid, thus confirming Liechti and Suida's results (*loc. cit.*). The authors are satisfied by repeated experiments that the soluble fatty acid of Turkey-red oil from olive oil, and that from oleic acid are absolutely identical, and that in each case the pure acid is not decomposed by boiling with water.

In order to compare the turkey-red oil from olive, cotton-seed and castor oil respectively, the authors prepared the "total fatty acids" from these Turkey-red oils; in order to do this, it was necessary to saponify the triglyceride and also to decompose the sulphates of the fatty acids. This was effected by first boiling the washed crude Turkey-red oil with potash, and then with dilute acid. The resulting fatty acids, of which those from cotton-seed and olive oils were solid whilst that from castor oil was fluid, were then examined by the method proposed by the authors in a former paper (this vol., p. 620). The results are expressed in the following table. It will be seen that the "acetyl-values" of the acids from olive and cotton-seed oils correspond with the conversion of the unsaturated acids in these oils into hydroxy-acids, whilst the number for castor oil remains nearly the same. The table also shows the "acetyl-values" of the fatty acids from different commercial Turkey-red oils and also for the insoluble and soluble portion of Turkey-red oil from castor oil.

The difference in the behaviour of olive oil and castor oil is explained by the different constitution of oleic and ricinoleic acid, the latter being an hydroxy-acid which reacts with sulphuric acid with the elimination of water forming a sulphate, which is again decomposed into the hydroxy-acid and sulphuric acid, whilst the former combines with sulphuric acid forming hydroxystearic sulphate. The acid from Turkey-red oil from olive oil does not take up any iodine, whilst the iodine value of the acid from Turkey-red oil from castor oil is 77·3, and that of the ricinoleic acid is 85·3. The authors conclude from this that Turkey-red oil from castor oil is of much greater value as a mordant than that from olive oil.

Turkey-red oil.	Fatty acids from Turkey-red oil.			Fatty acids from the original oil.
	"Acid value."	"Saponification value."	"Acetyl value."	"Acetyl value."
From olive oil	151·6	255·6	104·0	4·7
„ cotton-seed oil	178·7	231·4	52·7	16·6
„ castor oil	140·0	283·4	143·4	142·1
„ „ „ soluble	139·2	286·4	147·2	—
„ „ „ insoluble	153·5	278·5	125·0	—
„ Javal	152·0	301·0	149·0	—
„ The Apollo Candle Company, Vienna	141·1	291·3	150·2	—
Calculated for hydroxystearic acid	164·0	328·0	164·0	—
„ ricinoleic acid	165·0	330·0	165·0	—
„ dihydroxystearin	140·25	420·75	280·5	—

G. H. M.

Action of Sulphur Dichloride on Ethyl Acetoacetate. By A. Delisle (*Ber.*, **20**, 2008—2009).—When ethyl acetoacetate (2 mols.) is treated with sulphur dichloride, a vigorous reaction takes place with evolution of hydrogen chloride, and the whole solidifies to a crystalline mass. The new *compound*, which has the formula $C_{10}H_{14}O_6S$, crystallises from alcohol in thin, lustrous, colourless prisms, sparingly soluble in ether, insoluble in water, soluble in baryta-water with formation of a barium salt. It softens at 75°, and melts at 90—91°. N. H. M.

Constitution of Ethyl Propiopropionate. By A. Geuther (*Annalen*, **239**, 386—388).—As Israel (Abstr., 1886, 334) has recently shown that ethyl propiopropionate is decomposed by treatment with sodium ethoxide and ethyl iodide, yielding ethyl propionate and α-ethylpropionic acid or methylethylacetic acid, the author concludes that the constitution of ethyl propiopropionate is correctly represented by the formula OH·CEt : CMe·COOEt. W. C. W.

Action of Phosphoric Chloride on Chloralide. By R. Anschütz and A. R. Haslam (*Annalen*, **239**, 297—300).—Ethereal oxalates are converted into ethereal salts of dichloroglycollic acid by the action of phosphoric chloride (Abstr., 1886, 786 and 1011); but when chloralide is heated with phosphoric chloride at 290° for several days, the product is an oily liquid of the composition $C_5HCl_7O_3$. The new compound boils at 134—136° under 12 mm. pressure, and its density at 20° is 1·7426. W. C. W.

Dissociation of Hydrated Oxalic Acid. By H. Lescoeur (*Compt. rend.*, **104**, 1799—1800).—Crystallised oxalic acid readily

becomes anhydrous, its vapour-pressure at 45° being 10·6 mm. No intermediate hydrate is formed. In moist air, the dehydrated acid not only absorbs 2 mols. H_2O, but at 5° the absorption continues until the acid has the composition $H_2C_2O_4 + 2{\cdot}41H_2O$, and has a vapour-pressure of 5·5 mm. The vapour-pressures of the dihydrate at different temperatures are as follows :—

20°.	30°.	40°.	67°.	78·6°.
1·3 mm.	2·8	7·1	44·5	84·0

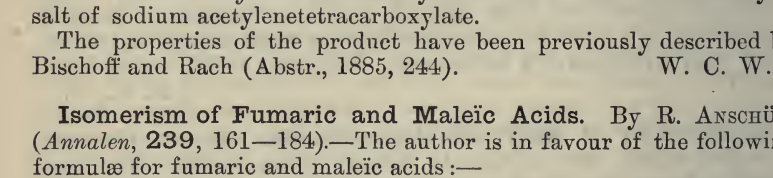
At 100°, the phenomenon becomes complicated by the decomposition of the oxalic acid, the vapour-pressure increases continually and becomes equal to 980 mm. after 24 hours.

In order to obtain oxalic acid of constant composition for the preparation of standard solutions, the ordinary crystals must be dried over sulphuric acid of 55° B. C. H. B.

Action of Iodine on Derivatives of Ethyl Sodiomalonate. By C. A. Bischoff and A. Hausdörfer (*Annalen*, **239**, 110—131).—By the action of iodine on ethyl benzylsodiomalonate in ethereal solution, *ethyl benzyliodomalonate* is produced. It is a colourless oil, and decomposes on hydrolysis, yielding benzaldehyde, alcohol, acetic acid, and carbonic anhydride, that is, the products of decomposition of ethoxybenzylmalonic acid. Iodine replaces the sodium in ethylsodiomalonate, and the product on saponification with alcoholic potash yields potassium ethylethoxymalonate, $OEt{\cdot}CEt(COOK)_2$, and on treatment with baryta-water yields barium ethyltartronate. *Ethyl dicarbontetracarboxylate* is formed by the action of iodine on the ethylic salt of sodium acetylenetetracarboxylate.

The properties of the product have been previously described by Bischoff and Rach (Abstr., 1885, 244). W. C. W.

Isomerism of Fumaric and Maleïc Acids. By R. Anschütz (*Annalen*, **239**, 161—184).—The author is in favour of the following formulæ for fumaric and maleïc acids :—



Fumaric acid. Maleïc acid.

His reasons for regarding maleïc acid as the dioxy-lactone of γ-hydroxycrotonic acid are as follows :—The formation of maleïc acid when trichlorophenomalic acid is decomposed by baryta, and the occurrence of maleïc and not fumaric acid in the products of decomposition of bromopyromucic acid, $\ll^{CBr{\cdot}CH(OH)}_{CBr——CO}\gg O$. The author, in conjunction with Wirtz, has just shown that maleïnanil is decomposed by baryta, yielding the salt of fumaranilic acid (p. 934). The relation between mesaconic and citraconic acids is probably similar to that between fumaric and maleïc acids—

$$COOH{\cdot}CH : CMe{\cdot}COOH$$

Mesaconic acid.

$$<\begin{matrix}CH : CMe\\ CO\text{——}O\end{matrix}>C(OH)_2 \text{ or } <\begin{matrix}CMe : CH\\ CO\text{——}O\end{matrix}>C(OH)_2.$$

Citraconic acid.

The conversion of maleïc into fumaric acid by the action of hydrochloric acid is explained by the following equation:—

$$COOH{\cdot}CH : CH{\cdot}C(OH)_2Cl - HCl = COOH{\cdot}CH : CH{\cdot}COOH.$$

This also explains why fumaric and maleïc acids yield the same product when treated with hydrobromic acid. W. C. W.

Conversion of Fumaric and Maleïc Acids into Aspartic Acid. By Engel (*Compt. rend.*, **104**, 1805—1807).—Fumaric or maleïc acid is heated for 20 hours at 140—150° with an excess of alcoholic ammonia, the ammonia is expelled, the residue dissolved in water, and the solution acidified with hydrochloric acid. After a short time, white crystals separate and are recrystallised from boiling water. Aspartic acid is the product in both cases; it crystallises in long, rhombic prisms which are identical with the inactive aspartic acid obtained by Dessaignes, and not with the active acid obtained from asparagin. The yield is not theoretical, owing to the fact that aspartic acid is somewhat readily decomposed when heated in sealed tubes at 140—150° with aqueous ammonia or even with water. If active aspartic acid is heated under these conditions for 20 hours, 60—70 per cent. of the acid is decomposed and the remainder becomes optically inactive. C. H. B.

Synthesis of Xeronic Acid from α-Dibromo-normal-butyric Acid. By G. Fromme and R. Otto (*Annalen*, **239**, 272—285).—By the action of molecular silver on α-dichloropropionic acid, Otto and Beckurts (Abstr., 1885, 753) obtained α-pyrocinchonic (dimethylfumaric) acid. By the same process, the authors convert α-dibromobutyric acid into xeronic and butyric acids. These acids are separated by the difference in the solubility of the calcium salts in hot water. The butyrate is more soluble than the xeronate. By the action of hydriodic acid at 180°, xeronic anhydride is converted into diethylsuccinic acid. This confirms the accuracy of Roser's hypothesis (Abstr., 1882, 1114) that xeronic acid is diethylfumaric acid.

The silver and copper salts of diethylsuccinic acids, $C_6H_{12}(COOAg)_2$ and $C_6H_{12}(COO)_2Cu + H_2O$, are amorphous powders sparingly soluble in hot water. W. C. W.

Action of Ethyl Oxalate on Acetone. By L. Claisen and N. Stylos (*Ber.*, **20**, 2188—2191).—*Ethyl acetopyruvate*, $CH_2Ac{\cdot}COOEt$, is formed by adding a mixture of acetone and ethyl oxalate drop by drop to an alcoholic solution of sodium ethoxide cooled in ice; much heat is developed, and a yellow crystalline sodium compound separates, which yields the ethyl salt on treatment with a dilute acid. It is a colourless oil of sp. gr. = 1·124 at 21°, boils at 134—135° under 40—41 mm., and at 213—215° under the ordinary pressure, and solidifies

to a crystalline mass melting at 18°. With ferric chloride, it gives a dark-red coloration showing a yellowish-red tinge; with phenylhydrazine, it forms a thick oil, and on treatment with aniline yields a liquid phenylimide; copper and zinc compounds were also obtained. Sulphuric acid dissolves the salt with a pale yellow colour, and on shaking the solution with ordinary benzene containing thiophen it gives an intense dark, red colour changing to violet-red. The *acid* has not been obtained pure, but is probably formed when the sodium compound of ethyl acetopyruvate is treated with water, and the product after treatment with a mineral acid is extracted with ether; this impure product is sparingly soluble in water, but cannot be crystallised from a hot solution, inasmuch as carbonic anhydride is evolved, and a crystalline compound, $C_9H_{12}O_6$, obtained, which melts at 90—91°.

W. P. W.

Carbamide-derivatives of Dibromopyruvic Acid. By E. Fischer (*Annalen*, **239**, 185—194).—*Dibromopyvureïd*, $C_4H_2O_2Br_2N_2$, is deposited in colourless crystals when equal weights of carbamide and dibromopyruvic acid are heated at 100° with sulphuric acid. The compound is sparingly soluble in alcohol, water, and acids; it dissolves in alkalis, but it is rapidly decomposed on boiling the solution. Ammonia converts dibromopyvureid into a sparingly soluble ammonium salt, which slowly changes into dibromopyvuramide and ammonium oxalate. The quinidine salt is sparingly soluble in cold water. *Tribromopyvurine*, $C_4H_3Br_3N_2O_3$, is prepared from dibromopyvureid by oxidation with nitric acid or by treatment with warm concentrated hydrobromic acid. It crystallises in colourless glistening plates soluble in hot alcohol, melts at 247° (uncorr.) with decomposition, and on treatment with ammonia splits up into bromoform and oxaluric acid. *Dibromopyvuramide*, $C_4H_5Br_2N_3O_2$, melts between 170° and 180° with decomposition. It is soluble in hot water and in hot alcohol, but the aqueous solution is decomposed on boiling. Ammonia at 100° eliminates the bromine and forms an amorphous compound. A warm solution of baryta-water decomposes dibromopyvuramide, forming tartronic acid and small quantities of mesoxalic acid and amidouracil.

W. C. W.

Sodium and Potassium Ethyl Tartrates. By Lasser-Cohn (*Ber.*, **20**, 2003—2004).—Iodine has no action on sodium ethyl tartrate. When treated with bromine, ethyl tartrate and sodium bromide are formed. When potassium ethyl tartrate is treated with iodine dissolved in benzene, potassium iodide, iodoform, and a resinous substance are formed.

N. H. M.

Synthesis and Constitution of Uric Acid. By J. Horbaczewski (*Monatsh. Chem.*, **8**, 201—207; comp. Abstr., 1883, 179; 1885, 1050). —When trichlorolactamide (1 part) and carbamide (10 parts) are melted together in small quantities over a small flame, a brownish-yellow mass is obtained, which when treated with potash, &c., as in the author's former method for the synthesis of uric acid (Abstr., 1883, 179) yields a white crystalline powder exhibiting all the properties, reactions, and the composition of uric acid. The yield of

uric acid by this method is not very good, this is accounted for by the partial decomposition of the acid when formed, and by the loss of the easily decomposable trichlorolactamide. This synthesis confirms the formula for uric acid suggested by Medicus, and shows it to be a diureide of acrylic acid, $CO<\begin{matrix}NH—C—CO—NH\\ \|\quad\quad\quad|\\ NH—C—NH—CO\end{matrix}$. G. H. M.

Solubility of Uric Acid. By C. Blarez and G. Denigés (*Compt. rend.*, **104**, 1847—1849).—The dissolved uric acid was estimated by means of potassium permanganate (this vol., p. 621).

The number of milligrams of uric acid dissolved by 100 grams of water at different temperatures is given by the equation—

$$x = 2 + 0{\cdot}15t + 0{\cdot}0020t^2 + 0{\cdot}000025t^3.$$

The following are some of the numbers actually observed:—

Temperature	0°	10°	20°	100°
Milligrams of uric acid in 100 grams water	2·0	3·7	6·0	62·5

The determinations are rendered difficult by the tendency of uric acid to form supersaturated solutions, and the formation of hydrated products, which absorb variable amounts of permanganate. If the solution is heated to a high temperature and then cooled, the proportion of permanganate absorbed by the cooled liquid increases with the time of cooling. Constant results can only be obtained by agitating the uric acid with water at the particular temperature at which the determination of solubility is to be made, care being taken that contact is not too prolonged, especially at high temperatures.

C. H. B.

Synthesis of Compounds of the Uric Acid Series. By R. Behrend (*Annalen*, **240**, 1—23).—*Nitromethyluracil*, $C_5H_5N_3O_4$, is prepared by gradually adding 4 grams of methyluracil to a mixture of 15 c.c. of fuming nitric acid and 15 c.c. of sulphuric acid. The temperature should not rise above 30—40°. The product is poured into water, and the crystalline precipitate recrystallised from water, from which it separates in prismatic crystals. It dissolves readily in hot water, sparingly in alcohol. Alkalis dissolve it with yellow colour. Potassium nitrouracilcarboxylate (*Annalen*, **229**, 32) is prepared by adding methyluracil to a mixture of fuming nitric and sulphuric acids, previously heated at 80°. The carboxylic acid separates on cooling; this product is dissolved in 100 c.c. of water, and 15 grams of caustic potash added. The potassium salt separates on cooling in lustrous plates. When this is heated at 170°, it is converted into potassium nitrouracil, from which nitrouracil is obtained by treatment with hydrochloric acid.

Hydroxyxanthin is obtained by adding zinc to a solution of nitrouracil in hot dilute hydrochloric acid. When cold, it is filtered, neutralised with sodium carbonate, treated with a slight excess of potassium cyanate, and made acid with hydrochloric acid, when the hydroxyxanthin separates as a white crystalline precipitate.

Potassium nitrouracil, $C_4H_2N_3O_4K + H_2O$, is prepared by neutralising a hot solution of nitrouracil with hydrogen potassium carbonate. It separates in pale yellow prisms. The *ammonium salt* forms aggregates of prismatic crystals, and is sparingly soluble. The *calcium salt* (with 6 mols. H_2O) forms large plates. The *barium salt* (with 5 mols. H_2O) crystallises in long slender needles of a slightly silky lustre. The *zinc* (with $3\frac{1}{2}$ mols. H_2O), *copper* (with 7 mols. H_2O), and *silver* salts are also described.

Nitrobromohydroxyuracil, $NO_2 \cdot CBr{<}\begin{matrix}CH(OH)\cdot NH\\ CO\cdot NH\cdot CO\end{matrix}{>}$, is formed when 10 grams of bromine is added to 6 grams of very finely powdered nitrouracil suspended in water and cooled with ice. After 24 hours, it is filtered, and the white precipitate washed with water and alcohol. It cannot be recrystallised, as it decomposes when warmed with water or alcohol. When distilled with steam, a brominated nitromethane and *nitrouracil-carbamide*, $C_5H_7N_5O_5$, are formed. The latter is also obtained by adding 1·5 gram of urea to a solution of 2 grams of nitrouracil in hot water. It is very sparingly soluble in water, and is decomposed by alkaline carbonates.

Amidouracilcarboxylic acid (Köhler, this vol., p. 128) is prepared by dissolving potassium nitrouracilcarboxylate in hot water, adding an alkaline solution of stannous chloride, filtering, and treating with hydrochloric acid. The yield is 80 per cent. of the theoretical.

Bromouracilcarboxylic acid, $C_5H_3N_2BrO_4 + 2H_2O$, is obtained by adding bromomethyluracil to fuming nitric acid so long as it dissolved readily. It crystallises from hot water in plates. It decomposes at above 170°. N. H. M.

Action of Phosphoric Sulphide on Ethyl Dimethylpyronedicarboxylate. By M. Guthzeit and W. Epstein (*Ber.*, **20**, 2111—2113).—*Ethyl thiodimethylpyronedicarboxylate*,

$$CS{<}\begin{matrix}C(COOEt)\cdot CMe\\ C(COOEt)\cdot CMe\end{matrix}{>}O,$$

is obtained when ethyl dimethylpyronedicarboxylate (this vol., p. 502) is heated with phosphoric sulphide at 100° for half an hour. It crystallises in orange needles, melts at 109—110°, and is insoluble in water, readily soluble in ether, hot alcohol, and benzene. The salt does not give the thiophen-reactions with isatin and phenanthraquinone, and on treatment with aqueous baryta yields acetone and barium acetate, carbonate and sulphide, together with a small quantity of a sparingly soluble red barium salt containing sulphur, whilst *ethyl thiophenyllutidinedicarboxylate*, $C_{19}H_{21}O_4SN$, is formed when it is treated with aniline in acetic acid solution. This crystallises in slender yellow needles, melts at 245°, dissolves in alcohol, and is identical with the compound obtained by the action of phosphoric sulphide on ethyl phenyllutidinedicarboxylate.

Lutidone when heated at about 160° with phosphoric sulphide yields *thiolutidine*, C_7H_9SN; this crystallises in needles, begins to fuse at 205°, melts at 210—215°, and is readily soluble in hot water and alcohol, insoluble in ether. W. P. W.

Thiophen-group. By N. Zelinsky (*Ber.*, **20**, 2017—2025).—*Metathioxen*, $C_4SH_2Me_2$ [$Me_2 = 2:4$], is obtained by distilling a mixture of 20 grams of α-methyllevulinic acid (Bischoff, *Annalen*, **206**, 319) and 30 to 35 grams of phosphorus trisulphide in a capacious retort. The fraction boiling below 160° is boiled for some hours with caustic potash, dried with calcium chloride, and distilled. It is a clear, colourless, strongly refractive oil, having an odour of petroleum. It boils at 137—138° (corr.); sp. gr. at 20° = 0·9956. The yield of pure product is 20 per cent. of the weight of the α-methyllevulinic acid. It shows the same colour reactions as thiophen. The *acetyl-derivative*, C_4SHMe_2Ac, is prepared by adding a mixture of 6 grams of metathioxen, 6 grams of acetic chloride, and 15 grams of light petroleum to 20 grams of light petroleum containing 8 grams of aluminium chloride in suspension. The whole is heated for a short time on a water-bath, the petroleum poured off, and the residue treated with cold water and steam-distilled. It is a clear liquid, boiling at 226—228° (uncorr.), has an odour of acetophenone, and becomes dark when exposed to air. It gives a red coloration with sulphuric acid and isatin. The *hydroxylamine-derivative* of the acetyl compound, $C_8H_{11}SNO$, crystallises from aqueous alcohol in thick needles melting at about 70°; the *phenylhydrazine-derivative*, $C_{14}H_{16}SN$, forms bright yellow needles melting at 70°.

Methylthiophencarboxylic acid, $C_4SH_2Me{\cdot}COOH$ [$Me : COOH = 2:4$ or $4:2$], is obtained, together with thiophendicarboxylic acid, by oxidising 1 gram of thioxen in a solution of 12 grams of sodium hydroxide, and 5·7 grams of potassium permanganate in 800 c.c. of water. After two days, the product is steam-distilled, and the distillate extracted with ether. It crystallises in needles melting at 118—119°, dissolves readily in ether, sparingly in water, and can be sublimed. The *calcium salt*, with $2\frac{1}{2}$ mols. H_2O, crystallises in plates.

Thiophendicarboxylic acid, $C_4SH_2(COOH)_2$ [$(COOH)_2 = 2:4$], is formed only in small quantity in the above experiment, and is prepared by oxidising the monocarboxylic acid; a portion of the latter always remains unattacked. It is readily soluble in hot water, and does not distil with steam; when heated at 280°, it sublimes with partial decomposition. The *silver salt* forms a curdy precipitate; the *methyl salt* crystallises in small plates and melts at 120—121°; the *ethyl salt* forms an oil which gradually crystallises, and melts then at 35—36°. When 5 grams of carbamic chloride is added to 3 grams of β-thiotolen dissolved in 10 grams of carbon bisulphide, the whole gradually treated with 5 grams of finely-powdered aluminium chloride, and then warmed on a water-bath, an amide is obtained which crystallises from hot water in needles melting at 119°. When the amide is saponified with alcoholic potash solution, the potassium salt of an acid melting at 143° is obtained, probably identical with Levi's γ-thiotolenic acid (Abstr., 1886, 540). When oxidised, this acid yields a dicarboxylic acid which is not identical with that described above; it shows the fluoresceïn reaction, and is therefore probably an ortho-derivative.

Dimethyllevulinic acid and *trimethylthiophen* were also prepared, but are not described. N. H. M.

Molecule of Crystalline Benzene. By A. Schrauf (*Ann. Phys. Chem.* **31**, 540—543).—Thomsen supposes that the arrangement of atoms is such that they lie in pairs of CH at the six corners of an octahedron. This arrangement does not accord with the fact discovered by Groth, that crystals of benzene belong to the trimetric system and are double refracting. These conditions may be satisfied in the simplest manner by removing two atoms H,H at opposite corners, and placing them one at each of two other opposite corners of the octahedron. This arrangement is shown to give the correct ratio of the axes. C. S.

Constitution of the Hydrocarbons C_nH_{2n} from Caucasian Petroleum. By W. Markownikoff and J. Spady (*Ber.*, **20**, 1850—1853).—The authors have examined the fraction boiling at 118—120°, and giving analytical results and vapour-density corresponding with the formula C_8H_{16}. Potassium permanganate did not cause oxidation either in acid or neutral solutions. When the hydrocarbon was boiled with sulphur, hydrogen sulphide was evolved, and small quantities of a heavy oil containing sulphur were formed, but the main liquid still boiled at 118—123°. When treated with a mixture of nitric and sulphuric acid, this liquid yielded a small quantity of trinitrometaxylene, whilst much of the original oil was recovered. The authors, therefore, consider that this petroleum fraction is, or contains, hexahydroxylene. When shaken successively with large quantities of sulphuric acid, metaxylene-mono- and di-sulphonic acids appear to be formed.

L. T. T.

Influence of Light and Temperature on Chlorination. By H. Gautier (*Compt. rend.*, **104**, 1714—1716).—Schramm has recently shown that the substitution of chlorine in the side-chains of benzene hydrocarbons can be effected even at 0°, provided the reaction takes place in sunlight. The author has made experiments in order to ascertain how far the laws of chlorination hold good for compounds other than hydrocarbons.

When a current of chlorine is passed into acetophenone at the ordinary temperature, substitution takes place rapidly with development of heat. The product is a dichloro-derivative with the chlorine exclusively in the methyl-group. If a slow current of the gas is passed into cooled acetophenone in diffused daylight, substitution still takes place almost exclusively in the side-chain, the yield of a derivative with chlorine in the nucleus amounting only to about 1 per cent. The result is the same in complete darkness, the temperature of the liquid exerting no influence.

Since the development of heat is mainly due to the formation of the monochlorine-derivative, the latter was treated with chlorine both in daylight and in the dark. The result was still the same.

It is evident that in this case light has no influence on the nature of the substitution. It does, however, accelerate the change, which requires four times as long in the dark as in diffused daylight. It would seem as if the presence of an electronegative group tends to prevent the introduction of an element of the same nature.

During the winter, *dichloracetophenone* (this vol., p. 141) was ob-

tained in crystals which melt at 19° and boil at 143° under a pressure of 25 mm. C. H. B.

Synthesis of Aromatic Alkyl Polysulphides. By R. Otto (*Ber.*, **20**, 2089).—When a warm alcoholic solution of benzenesulphinic acid is treated with hydrogen sulphide, a thick yellow oil of unpleasant odour separates, consisting chiefly of *phenyl tetrasulphide*. This compound is readily reduced to the bisulphide by the action of colourless ammonium sulphide in the cold. Paratoluenesulphinic acid yields *toluene tetrasulphide* when similarly treated; it crystallises in small scales, melts at 75°, and is not reduced by ammonium sulphide.

Benzenesulphonic chloride also yields phenyl polysulphides under similar conditions. W. P. W.

Chlorine-derivatives of Phenyl Methyl Ether (Anisoïl). By L. Hugounenq (*Compt. rend.*, **104**, 1807—1808).—When a current of chlorine gas is passed over phenyl methyl ether mixed with an equivalent quantity of ethyl alcohol, a solid product is obtained, crystallising from alcohol in long, white needles, which are soluble in ether, chloroform, benzene, carbon bisulphide, and glacial acetic acid. It melts at 59—60°, sublimes readily even at the ordinary temperature, and boils without decomposition at 240°, under a pressure of 738·2 mm. It is a trichloro-derivative, and is not attacked by boiling alcoholic potash, which indicates that substitution has taken place in the benzene-ring only. If the anisoïl is heated and treated with chlorine in presence of iodine, it yields another trichloro-derivative, which forms small needles melting at 56°. Other chlorine-derivatives and various oxidation products have been obtained, and will be described subsequently. C. H. B.

Carvole-derivatives. By H. Goldschmidt and E. Kisser (*Ber.*, **20**, 2071—2078; compare this vol., p. 475).—If carvole is treated with hydrogen bromide, *hydrobromocarvole*, $C_{10}H_{15}OBr$, is obtained as a thick oily compound, which decomposes at about 50°, and resinifies in the moist state with the evolution of hydrogen bromide. The *oxime*, $C_{10}H_{15}Br : NOH$, is formed by acting on hydrobromocarvole with the theoretical quantity of hydroxylamine, or by saturating a solution of carvoxime in methyl alcohol with hydrogen bromide; it crystallises from light petroleum in colourless, glistening prisms, and from alcohol in tufts of needles, melts at 116°, and when allowed to remain for some time darkens in colour, and eventually forms a viscid mass. The *phenylhydrazide*, $C_{10}H_{15}Br : N_2HPh$, crystallises in slender, yellow needles, and melts at 119°.

Isocarvoxime, $C_{10}H_{14} : NOH$, is obtained, together with a small quantity of carvoxime, when hydrobromocarvole or hydrobromocarvoxime in alcoholic solution is treated with an excess of hydroxylamine. It crystallises in needles, melts at 142—143°, and is sparingly soluble in alcohol. Isocarvoxime dissolves in acids and alkalis, and is more basic in its properties than carvoxime, but unlike that base it does not form additive compounds with hydrogen

chloride and hydrogen bromide. The *benzoyl*-derivative forms stellate, white, glistening scales, melts at 112°, and is readily soluble in alcohol, ether, and benzene.

The authors have not succeeded in obtaining an isomeride of carvole corresponding with isocarvoxime from either hydrochlorocarvole or hydrobromocarvole, and find that carvole and carvacrol are the end-products when the elements of hydrogen bromide are separated from the latter compound by repeated distillation, by heating with a mixture of anhydrous sodium acetate and acetic acid, or by the action of alcoholic potash in the cold. Isocarvoxime, when heated with dilute sulphuric acid, yields not the expected isocarvole (comp. Abstr., 1885, 1058) but carvacrol, hydroxylamine, and a compound, $C_{10}H_{15}NO$, isomeric with carvoxime. This crystallises from hot water in glistening, transparent prisms, melts at 94°, has an odour resembling that of indole, and is insoluble in cold water, soluble in ether.

The remainder of the paper is devoted to a discussion of the possible formulæ for isocarvoxime, and of these the formula

$$CPr\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}CH\cdot C(NOH) \\ CH_2\text{——}CH\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix}CMe$$

is adopted as the most probable. W. P. W.

Bromine-derivatives of Resorcinol. By J. Zehenter (*Monatsh. Chem.*, **8**, 293—298).—*Monobromoresorcinol*, $C_6H_3Br(OH)_2$, is obtained by boiling monobromo-α-dihydroxybenzoic acid (1 part) with water (5 parts) for some hours in a reflux apparatus, adding excess of dilute sulphuric acid, and extracting with ether. The ethereal extract is then treated with a little dilute ammonium carbonate to remove any unaltered acid, and, after separation, slowly evaporated. The monobromoresorcinol remains as a solid crystalline mass, which, when purified, forms slightly yellow, more or less nodular groups of crystals. It melts at 91°, and cannot be sublimed without decomposition; it is readily soluble in water and ether, less so in alcohol, chloroform, benzene, &c. The aqueous solution gives with ferric chloride a bluish-violet coloration, which, after a time, gives place to a reddish-brown precipitate. It reduces alkaline silver solutions; with bromine-water, it gives a precipitate of tribromoresorcinol. When heated in a sealed tube with water, it gives up the whole of its bromine. When heated with water, potassium carbonate and tin chloride, it gives resorcinol and α-dihydroxybenzoic acid.

Dibromoresorcinol, $C_6H_2Br_2(OH)_2$, is prepared by adding to resorcinol suspended in carbon bisulphide sufficient bromine dissolved in the same solvent, the greater part of the resorcinol is dissolved, and hydrogen bromide is given off, the liquid is quickly filtered, and the filtrate sets after a time to a crystalline mass. When purified by recrystallisation from water, dibromoresorcinol forms long, white needles, melts at 110—112°, and sublimes without decomposition. The air-dried crystals contain one mol. H_2O. Dibromoresorcinol is sparingly soluble in cold water, readily in hot water, alcohol, and ether; with ferric chloride, the aqueous solution gives a pure blue coloration, which, after a time, gives place to a dark pre-

cipitate; with neutral and basic lead acetate, it gives a white precipitate; with bleaching powder, a violet coloration, which changes first to red and then to gold. Bromine-water throws down a precipitate of tribromoresorcinol. It is soluble in alkalis, and is reprecipitated on adding an acid to the solution. In other respects, it resembles the monobromoresorcinol in behaviour.

This dibromoresorcinol differs from α-dibromoresorcinol prepared by Hofmann from eosin (this Journ., 1875, 571), and also from β-dibromoresorcinol previously described by the author (*loc. cit.*), both in its higher melting point, its reaction with ferric chloride, and also its readier solubility in water. From experiments made with α- and β-dibromoresorcinol, the author concludes that they are identical. G. H. M.

Action of Chlorine and Bromine on Pyrogallol. By A. Hantzsch and K. Schniter (*Ber.*, **20**, 2033—2040).—When chlorine is passed into an aqueous or alkaline solution of pyrogallol, and the product after removal of the excess of chlorine by a current of air is treated with ether, an oil is obtained which contains chlorine, is acid in reaction, and is soluble in water. It cannot be distilled unchanged, and is readily reduced to pyrogallol by the action of zinc and sulphuric acid. Leucogallol, obtained by Stenhouse and Groves (this Journ., 1875, 704), by chlorinating pyrogallol in acetic acid solution, has the formula $C_{18}H_6Cl_{12}O_{12} + 2H_2O$ originally ascribed to it, and yields *trichloropyrogallol*, $C_6H_3Cl_3O_3 + 3H_2O$, when dissolved in water and treated with zinc-dust in small portions at a time, rise of temperature being avoided. Trichloropyrogallol crystallises in long, white needles, and melts at 75°, whilst the anhydrous substance melts at about 185° with decomposition. It is very readily soluble in alcohol, ether, and chloroform, soluble in hot water, and dissolves in ammonia with a bright yellow colour. The aqueous solution gives insoluble precipitates of varying colours with most metallic salts, and ammoniacal silver nitrate yields with it a mirror of silver. The *barium* salt, $(C_6Cl_3O_3)_2Ba_3 + 6H_2O$, forms indistinct crystals; the *copper* salt, $(C_6Cl_3O_3)_2Cu_3 + 6H_2O$, is an amorphous green powder. The *acetyl*-derivative, $C_6Cl_3O_3Ac_3$, crystallises in slender needles, melts at 122°, is soluble in alcohol, ether, and benzene, insoluble in water, and is very stable towards sulphuric and nitric acids. Leucogallol, on account of the ease with which it is reduced, cannot be regarded as a derivative of a hydrocarbon, $C_{18}H_{18}$, and is most probably formed of three benzene molecules united by oxygen-atoms. With hydroxylamine hydrochloride, it yields a nitrogenous compound which gives Liebermann's reaction, and also reacts with phenylhydrazine acetate, but owing to their great instability neither compound has been obtained pure.

Mairogallol (*loc. cit.*), although it differs from leucogallol by reason of its insolubility in water and greater stability, yields trichlorpyrogallol under similar conditions.

Xanthogallol (Stenhouse, this Journ., 1875, 1) is neither reduced by sodium amalgam nor by zinc and sulphuric acid, but yields *trihydroxyxanthogallol*, $C_{18}H_4Br_{11}O_6(OH)_3$, when treated with dilute

aqueous soda. The *barium* salt has the formula $(C_{18}H_4Br_{11}O_9)_2Ba_3$; the *acetyl*-derivative, $C_{18}H_4Br_{11}O_9Ac_3$, crystallises in nacreous scales, and is soluble in all ordinary solvents, water excepted. Both xanthogallol and the trihydroxy-derivative yield compounds with phenylhydrazine acetate.

The second portion of the paper is devoted to a discussion of the probable constitution of these pyrogallol-derivatives, and in conclusion the authors state that the product obtained by Stenhouse on brominating bromanilic acid, and to which the formula $C_6HBr_{11}O$ was ascribed, is perbromacetone. W. P. W.

Anilic Acids. By S. Salzmann (*Ber.*, **20**, 1997—1999).—Hantzsch showed (this vol., p. 719) that the acid formed by the bromination of quinonedihydroxyparadicarboxylic acid, which contains both bromine-atoms in the para-position, is identical with ordinary bromanilic acid. By heating symmetrical tribromophenol with fuming sulphuric acid at 100—115°, the third possible bromanilic acid is obtained in which the bromine has the meta-position; this also seems to be identical with ordinary bromanilic acid. Bromanil is also formed in the reaction. The author considers that the chemical identity of the three acids is not established, and refers to α- and β-thiophencarboxylic acids as examples of compounds possessing the same physical properties. N. H. M.

Nitranilic Acid from Chloranil. By J. U. Nef (*Ber.*, **20**, 2027—2031).—When a hot solution of chloranil in acetone is gradually added to a concentrated aqueous solution of potassium or sodium nitrite heated at 80—90°, a dark reddish-brown coloration is at first produced, and after a short time a dark-yellow crystalline separation of the corresponding salt of nitranilic acid is obtained (Abstr., 1883, 465). The potassium salt forms microscopic crystals, which are probably monoclinic, and show feeble dichroism; the sodium salt forms characteristic dark-red monoclinic octahedra, $a : b : c = 0{\cdot}9463 : 1 : 0{\cdot}98489$; $\beta = 87° 5'$, and is strongly dichroic. All attempts to isolate the reddish-brown intermediate product have failed.

The action of a concentrated aqueous solution of potassium cyanide on chloranil dissolved in acetone results in the formation of several products, of which one crystallises well from acetic acid, and seems to have the formula $C_6(OH)_2Cl_2(CN)_2$. W. P. W.

Cholesterin. By B. Rayman (*Bull. Soc. Chim.*, **47**, 898—901).—The analogy of cholesterin to camphor is confirmed by the absence of any action when it is treated with hydroxylamine. The author failed in his attempts to prepare a sodium cholesterate, as also to prepare the cholesterin ether, $(C_{26}H_{43})_2O$. On heating cholesterin with acetic anhydride in a reflux apparatus, and cooling, *cholesterin acetate* separates in flocks; on crystallisation from benzene, it forms groups of needles which melt at 113° and decompose at a somewhat higher temperature, losing acetic acid; water acts on it in a similar manner.

Cholesteryl chloride may be prepared by heating cholesterin with

phosphoric chloride; it forms small scales and melts at 96°. On slowly evaporating the ethereal solution, it exhibits a fine violet fluorescence.

Cholesteryl chloride dibromide, $C_{26}H_{43}ClBr_2$, may be prepared by gradually adding bromine to an ethereal solution of cholesteryl chloride, when it is precipitated as a heavy white powder; it is insoluble in ether but soluble in most other solvents, and crystallises from its solution in carbon bisulphide in large, colourless crystals; it melts at 128° and is decomposed when heated to 158°. By digestion with sodium ethoxide or isobutoxide, or with a solution of potassium hydroxide, the bromine is removed and cholesteryl chloride regenerated.

By the action of potassium chlorate and hydrochloric acid on cholesterin an amorphous substance which appears to have the composition $C_{26}H_{41}Cl_2O_3$ is formed. The reduction of nitro-derivatives of cholesterin by zinc powder has not yielded any satisfactory results.

A. P.

Combination of Aniline with Chromic Acid. By C. Girard and L. L'Hote (*Compt. rend.*, **104**, 1725—1727).—When aniline is mixed with free chromic acid, oxidation takes place and no chromate is obtained. If, however, equal volumes of well-cooled saturated solutions of potassium dichromate and aniline hydrochloride are mixed together, a yellow crystalline precipitate is formed which must be immediately separated and drained by means of a filter-pump, then washed with small quantities of cold water, and dried on a porous plate over sulphuric acid in a vacuum. Sodium and ammonium dichromates give similar results.

The crystals are yellow monoclinic prisms which act strongly on polarised light and have a bright green lustre. They have the composition $2NH_2Ph,H_2Cr_2O_7$, are slightly soluble in cold water, and are decomposed by boiling water. When moist, they decompose on exposure to air and light, but remain unaltered if dry. They are very slightly soluble in alcohol, which they gradually convert into aldehyde. The compound decomposes when heated to a moderate temperature, and it burns with formation of chromic oxide when ignited or struck on an anvil. It takes fire in contact with fuming nitric acid, and if moistened with concentrated sulphuric acid it burns like pyrophoric copper. When mixed with alkalis and agitated with ether or benzene, it gives up aniline. When treated with water, it yields violet colouring matters similar to mauve.

C. H. B.

Phenylparatoluidine. By A. Bonna (*Annalen*, **239**, 55—64).—*Phenylparatoluidine* melts at 85—86° and boils at 317—318° (thermometer immersed in vapour). The nitroso-compound, $NPh(C_7H_7)\cdot NO$, is deposited from alcohol in yellow needles, soluble in ether and benzene. It melts at 82°. On the addition of bromine to the alcoholic solution, nitrosobromophenyltoluidine, $C_{13}H_{11}BrN_2O$, is deposited. On recrystallisation from ether or chloroform, it forms yellow needles melting at 166°. The acetic derivative is formed when acetic chloride is added to a solution of phenyltoluidine in benzene, and also by the action of acetic anhydride on phenyltoluidine at 200°. The acetic derivative melts at 51°, and is freely soluble in alcohol and

ether. On exposure to bromine-vapour, a monobromo-compound, $C_{13}H_{11}BrNAc$, is obtained. This substance crystallises in plates and melts at 72°. When phenylparatoluidine is exposed to the action of bromine-vapour at the ordinary temperature, the base unites directly with bromine, forming the compound $C_{13}H_{13}NBr_4$. This substance melts at 135°, and dissolves in ether, benzene, and chloroform.

Tetrabromophenylparatoluidine, $C_{13}H_9Br_4N$, is deposited on mixing an alcoholic solution of phenyltoluidine with the theoretical quantity of bromine diluted with glacial acetic acid; it melts at 156°. By the action of excess of bromine at 280° and 310°, compounds containing 7 and 11 bromine-atoms are obtained: $C_{13}H_6Br_7N$ melts at 185°, and $C_{13}H_2Br_{11}N$ melts at 296°. A compound of the composition $C_{13}H_6Br_7N$ is formed by the action of bromine-vapour on the base exposed to bright sunlight. This substance melts at 254°, crystallises in colourless needles, and dissolves in ether and light petroleum.

Phenylmethylacridine, formed by the action of zinc chloride and benzoic acid on phenylparatoluidine at 260°, is a white crystalline substance soluble in alcohol, benzene, and ether with greenish-blue fluorescence. It melts at 135—136°. The *hydrochloride* forms yellow needles, freely soluble in alcohol and water. On the addition of sodium sulphite to the aqueous solution of the hydrochloride, the *sulphite*, $(C_{20}H_{15}N)_2SO_3H_2$, is deposited as an orange precipitate. The red-coloured needles of the *picrate*, $C_{20}H_{15}N + C_6H_2(NO_2)_3OH$, dissolve in warm alcohol. The *hydriodide*, $C_{20}H_{15}NHI$, is precipitated on the addition of potassium iodide to a solution of the hydrochloride. On oxidation with dichromate mixture phenylmethylacridine yields a monocarboxylic acid, $C_6H_4\langle\begin{smallmatrix}CPh\\|\\N\end{smallmatrix}\rangle C_6H_3\cdot COOH$. The acid melts with partial decomposition between 252° and 255°. The silver salt, $C_{20}H_{12}NO_2Ag$, and the barium salt, $(C_{20}H_{12}NO_2)_2Ba$, are crystalline.

Dimethylacridine is formed by the action of zinc chloride and glacial acetic acid on phenylparatoluidine at 220°. It melts at 122—123°, dissolves freely in alcohol and benzene, and forms yellow needles or prisms. The *hydrochloride*, *hydriodide*, and *picrate* are crystalline salts soluble in alcohol. The hydrochloride also dissolves in water.

W. C. W.

Cyananiline, Cyanphenylhydrazine, and Analogous Compounds. By A. Senf (*J. pr. Chem.* [2], **35**, 513—541).—Cyananiline is prepared by passing cyanogen through a solution of 10 grams of aniline in 30 grams of absolute alcohol mixed with 60 grams of water. The crystals thus obtained are treated with dilute sulphuric acid to dissolve the cyananiline, which is subsequently precipitated by ammonia. A red crystalline substance remains undissolved in the acid. Cyananiline is also formed by heating oximidoether, $OEt\cdot C(NH)\cdot C(NH)\cdot OEt$, (Pinner and Klein, Abstr., 1879, 46), with aniline. This reaction shows the correctness of the constitution $NHPh\cdot C(NH)\cdot C(NH)\cdot NHPh$ for cyananiline. Dry nitrous anhydride converts cyananiline suspended in absolute ether into the nitrate; this decomposes violently when melted, yielding phenylcarbylamine. When a solution of cyananiline in acetic acid and water is treated with nitrous acid, phenyl-

carbylamine, oxanilide, and α-dinitrophenol are obtained; the latter is formed by the action of nitrous acid on oxanilide. Sodium amalgam reduces cyananiline to ammonia, aniline, and formic acid. When bromine is added to a solution of cyananiline in chloroform at 0°, the compound $C_2(NH)_2(NH{\cdot}C_6H_4Br)_2,HBr,Br_2$ separates; the latter dissolves readily in water; when distilled with steam, tribromaniline is formed; if ammonia is added to the solution of the bromine-compound in dilute sulphuric acid, the compound $C_{14}H_{12}N_4Br_2$ is formed. This crystallises from benzene in white plates. *Paradibromocyananiline*, $C_2(NH)_2(C_6H_4Br{\cdot}NH)_2$, is obtained by boiling a solution of cyananiline in glacial acetic acid with bromine. The crystalline product is dissolved in water and precipitated with ammonia. It is also formed when parabromaniline is treated with cyanogen. Phthalic anhydride acts on cyananiline at 150°, yielding phthalanile.

Cyanxylide, $C_2(NH)_2(NH{\cdot}C_6H_3Me_2)_2$, is a yellow substance soluble in alcohol.

No additive products of cyanogen with methylaniline and diphenylamine could be obtained.

Cyanmetanitraniline, $C_2(NH)_2(NH{\cdot}C_6H_4{\cdot}NO_2)_2$, prepared by the action of cyanogen on metanitraniline, is a brown substance, soluble in alcohol.

Cyanphenylhydrazine, $C_{14}H_{16}N_6$, is prepared by passing cyanogen through an alcoholic solution of pure phenylhydrazine until the solution begins to become opaque; the whole is left for 12 hours. It melts at 225°, and dissolves sparingly in alcohol. It can also be obtained from cyananiline and phenylhydrazine.

When a solution of cyananiline in chloroform is boiled with phenylhydrazine, and the product is left for 24 hours, the compound $CHCl(C_{14}H_{15}N_6){\cdot}N_2H_2Ph,2HCl$ is formed. This crystallises in yellow matted needles melting at 200—212°; it is readily soluble in cold water and alcohol, insoluble in ether, benzene, and chloroform.

Cyanogen has no action on diphenylhydrazine, the constitution of cyanphenylhydrazine is therefore $C_2(NH)_2(NH_2 : NPh)_2$.

Cyanphenylhydrazine hydrochloride is prepared by passing dry hydrogen chloride through a solution of the base in absolute alcohol; it is very unstable and decomposes in moist air. It dissolves very readily in alcohol.

When cyanphenylhydrazine is warmed with dilute hydrochloric acid, and the product treated with ammonia, the compound

$$NPh : NH_2{\cdot}CO{\cdot}C(NH){\cdot}NH_2 : NPh$$

is obtained. The latter crystallises in greyish-white plates melting at 180°; it dissolves very readily in alcohol and ether, very sparingly in boiling benzene and chloroform. The *hydrochloride* is a yellow substance melting at about 120°.

Cyanphenylhydrazine is decomposed by dilute hydrochloric acid at 160° into phenylhydrazine hydrochloride, ammonium chloride, carbonic anhydride, and carbon oxide. N. H. M.

Hexa-derivatives of Benzene. By R. Nietzki (*Ber.*, **20**, 2114—2118).—A better method for nitrating diacetylmetaphenylenedi-

amine than that previously described (this vol., p. 476) is to mix one-fifth its weight of carbamide nitrate with the base, and to gradually add the mixture to six times its volume of pure nitric acid cooled to −2°; ordinary fuming nitric acid (sp. gr. = 1·52) cannot be substituted for the pure acid, since the mononitro-derivative is the sole product of its action even at 20°.

The *nitrate* of diimidodiamidobenzene, $(NH)_2C_6H_2(NH_2)_2,2HNO_3$, is obtained by treating a solution of tetramidobenzene (1 part) in water (15 parts) with ordinary nitric acid (2 parts) and afterwards with an excess of ferric chloride. It crystallises in small, green needles, and when gradually added to an excess of sulphuric acid cooled to 10° dissolves with a reddish-violet colour rapidly changing to a brownish-yellow, and on the addition of ice *dinitrodiamidoquinone*, $C_6H_4N_4O_6$, crystallises from the solution in stellate groups of dark-yellow needles. This compound is practically insoluble in all ordinary solvents, and is a feeble base yielding salts readily decomposed by water. Dinitrodiamidoquinone yields potassium nitranilate when heated with dilute aqueous potash, and nitramidotetrahydroxybenzene on treatment with acid stannous chloride, whilst its solution in strongly acid stannous chloride gives on saturation with hydrogen chloride the hydrochloride of a new base crystallising in colourless scales, and having the composition $C_6H_{14}N_4Cl_4$. On the reduction of dinitrodiamidoquinone, the tetrahydrochloride of tetramidodihydroxybenzene or tetramidoquinol is obtained. In its properties, this base shows much similarity to diamidotetrahydroxybenzene (Abstr., 1885, 779), thus it is converted by oxidising agents into compounds containing less hydrogen, and when boiled in alkaline solution with manganese dioxide yields croconic acid. The sulphate is sparingly soluble in water, and the base on exposure to the air rapidly assumes a violet colour. W. P. W.

Action of Aromatic Diamines on Sugars. By P. Griess and G. Harrow (*Ber.*, **20**, 2205—2213; compare this vol., p. 475).—*Digluco-orthodiamidobenzene*, $C_6H_4(N:C_6H_{12}O_5)_2 + 2H_2O$, is obtained when aqueous solutions of dextrose (2 mols.) and orthodiamidobenzene (1 mol.) are mixed in the absence of acids. It crystallises in slender, white needles, has a bitter taste, carbonises when heated, and is readily soluble in cold water, nearly insoluble in strong spirit and in ether. Its aqueous solution is strongly lævorotatory, reduces Fehling's solution, and gives an intense yellowish-red coloration with ferric chloride. When heated with alkalis and mineral acids, it is decomposed seemingly without a preliminary resolution into its components.

Anhydrogluco-orthodiamidibenzene,

$$C_6H_4<\overset{N:CH}{\underset{\quad N}{\quad}}>C\cdot[CH(OH)]_3\cdot CH_2\cdot OH + 2H_2O,$$

is formed, together with gluco-orthodiamidobenzene, by the action of dextrose on diamidobenzene in presence of acids, and separates first on crystallisation. It forms lustrous, white needles, has a bitter taste, reduces Fehling's solution, dissolves readily in boiling alcohol or water, but crystallises out almost entirely on cooling, and is insoluble in

ether. It shows very feeble basic properties, and is decomposed when boiled with acids or alkalis, with formation of an insoluble, red, basic compound.

Gluco-orthodiamidobenzene,

$$C_6H_4<\begin{matrix}NH\\NH\end{matrix}>CH\cdot CO\cdot[CH(OH)]_3\cdot CH\cdot OH,$$

forms small, white plates of slightly bitter taste, moderately soluble in cold water and alcohol, nearly absolutely insoluble in ether. It has strongly pronounced basic properties; the hydrochloride crystallises in plates, and is very readily soluble in water. It is not decomposed by acids or alkalis, and does not reduce Fehling's solution.

The action of orthotoluylenediamine on dextrose has been described by Hinsberg (this vol., p. 476). The authors had independently obtained the same results, but have further prepared *glucometapara-diamidotoluene*, $C_6H_3Me<\begin{matrix}NH\\NH\end{matrix}>C_6H_{10}O_5$, crystallising in small, white nodules moderately soluble in water.

Gluco-γ-diamidobenzoic acid,

$$C_6H_{10}O_5<\begin{matrix}NH\\NH\end{matrix}>C_6H_3\cdot COOH\ [NH:NH:COOH=3:2:1],$$

prepared by mixing boiling aqueous solutions of dextrose and γ-diamidobenzoic acid, crystallises is small, longish three- to six-sided plates, has scarcely any taste, melts with decomposition when heated, and has a feeble acid reaction. It is sparingly soluble in hot water, insoluble in alcohol and ether, and is not decomposed by boiling with hydrochloric acid or with baryta-water. The hydrochloride crystallises in indistinct white plates. The barium salt is obtained as a snow-white powder. Both acid and alkaline solutions are dextrorotatory.

Malto-γ-diamidobenzoic acid, $C_{12}H_{20}O_{10}<\begin{matrix}NH\\NH\end{matrix}>C_6H_3\cdot COOH$, obtained by the action of γ-diamidobenzoic acid on maltose, crystallises in short, white microscopic needles, moderately soluble in hot water, sparingly in cold, and insoluble in alcohol and ether. Its barium salt is described. A. J. G.

Action of Aniline Hydrochloride on Ethylene Cyanide. By R. Blochmann (*Ber.*, **20**, 1856—1861).—When a mixture of aniline hydrochloride and ethylene cyanide is melted, reaction takes place, and the temperature of the mass rises to above 200°, much charring taking place. The compound formed is *diphenylsuccinimidine hydrochloride*, $C_2H_4<\begin{matrix}C(NH)\\C(NPh)\end{matrix}>NPh,HCl$. If excess of aniline hydrochloride is used, the temperature does not rise so high, charring does not occur, and a better yield is obtained. The hydrochloride crystallises in glistening needles, and is soluble in boiling water and alcohol, but in each case with partial decomposition. The *platinochloride*, $(C_{16}H_{15}N_3)_2,H_2PtCl_6$, is orange coloured and crystalline. The free *base* forms pale-green crystals insoluble in water, soluble in alcohol. The *hydrobromide*, *hydriodide*, *sulphate*, and *nitrate* crystallise in needles.

When the hydrochloride is boiled with water, it is decomposed into succinanil, $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NPh$, aniline, and ammonium chloride. With boiling alcohol, *hydrogen ethyl phenylsuccinimidate*,

$$NPh:C(OH)\cdot C_2H_4\cdot C(OEt):NH,$$

aniline, ammonium chloride, and seemingly small quantities of ethylaniline are formed.

Diphenylsuccinimidine unites readily with methyl iodide to form an ammonium base. L. T. T.

Chlorinating by means of Acetic Chloride. By P. Becker (*Ber.*, **20**, 2006—2008).—When azobenzene is heated with acetic chloride at 160—170° for three to four hours, a product is obtained consisting of paradichlorazobenzene (Heumann, this Journal, 1873, 167) and parachloracetanilide. The latter when recrystallised from hot water melts at 175·5—176° (not 172·5°, Beilstein and Kurbatow, *Annalen*, **182**, 99). N. H. M.

Orthazoxytoluene. By A. L. Guitermann (*Ber.*, **20**, 2016—2017).—The compound obtained by G. Schultz (*Ber.*, **17**, 468) by the action of stannous chloride on orthazotoluene is shown to be orthazoxytoluene, $(C_7H_7N)_2O$, identical with the compound obtained by Klinger and Pitschke (Abstr., 1886, 53). When reduced in acid solution, orthotoluidine (m. p. 129°, not 112°) is formed.

N. H. M.

The Hydrazines. By E. Fischer (*Annalen*, **239**, 248—252).—Phenylhydrazine and methylphenylhydrazine are decomposed by the prolonged action of zinc-dust and hydrochloric acid, yielding ammonia and aniline or methylaniline respectively.

Acetomethylphenylhydrazine, NMePh·NHAc, melts at 92—93°, and distils with slight decomposition. It is soluble in alcohol, benzene, and in hot water. *Acetodimethylphenylhydrazine*, NMePh·NMeAc, is prepared by the action of methyl iodide on the product of the action of sodium on a solution of acetomethylphenylhydrazine in xylene. The new compound forms colourless crystals, melts at 68°, and distils without decomposition. It does not reduce alkaline, copper, or silver solutions, nor is it attacked by alkalis. It is decomposed by boiling with hydrochloric acid, yielding acetic acid and monomethylaniline.

W. C. W.

Compounds of Phenylhydrazine with Acrolein, Mesityloxide, and Allylbromide. By E. Fischer and O. Knoevenagel (*Annalen*, **239**, 194—206).—The compound $C_9H_{10}N_2$, which Fischer (Abstr., 1886, 806) obtained by the action of phenylhydrazine on acraldehyde in ethereal solution, is *phenylpyrazoline*. This substance melts at 51—52°, and boils at 273—274°. It is freely soluble in alcohol, ether, benzene, in hot water, and also in strong hydrochloric acid; in the latter case, the greater part is reprecipitated on diluting the acid with water. The dilute acid solution exhibits the characteristic violet or blue coloration with potassium dichromate. When bromine acts on phenylpyrazoline in the presence of chloroform, a

yellow crystalline compound is formed which gives off hydrogen bromide on exposure to the air. On recrystallisation from hot alcohol, colourless crystals of *dibromophenylpyrazoline*, $C_9H_8Br_2N_2$, are deposited. This substance melts with decomposition at 92—93°, and dissolves in hot alcohol, chloroform, ether, and glacial acetic acid. It is converted into *bromethoxyphenylpyrazoline*, $C_{11}H_{13}N_2BrO$, by alcoholic potash. The new compound melts at 65—66°, and dissolves in ether, chloroform, and hot alcohol, and light petroleum. It is decomposed by heating with strong hydrochloric acid, yielding ethyl chloride and *bromohydroxyphenylpyrazoline*, $C_9H_7N_2BrO$, a crystalline compound melting at 214°. The pyrazoline compound forms crystalline salts with ammonium, sodium, and barium. The barium salt is sparingly soluble in hot water.

Sodium amalgam reduces the aqueous solution of bromohydroxyphenylpyrazoline to *hydroxyphenylpyrazoline*, $C_9H_8N_2O$, a crystalline compound melting at 152—153°. The compound is soluble in strong hydrochloric and acetic acids, in dilute alkalis, and also in chloroform, benzene, and hot alcohol.

Phenylhydrazine unites with mesityl oxide, forming *trimethylphenylpyrazoline*, $C_{12}H_{16}N$, an oily liquid, soluble in ether, alcohol, benzene, chloroform, and in dilute acids. The acid solutions exhibit the pyrazoline reaction with potassium dichromate. The *platinochloride*, $(C_{12}H_{16}N_2)_2,H_2PtCl_6$, is crystalline, and almost insoluble in water.

Allylphenylhydrazine, $C_9H_{12}N_2$, is formed by the action of allyl bromide on phenylhydrazine largely diluted with ether. At the commencement of the operation, the temperature must not exceed 20° to 25°. The product is a pale oil boiling at 172° under 60 mm. pressure. It is soluble in dilute acids, and reduces Fehling's solution. On treating the ethereal solution with yellow mercuric oxide, it is converted into *azophenylallyl*, $C_9H_{10}N_2$, which closely resembles azophenylethyl in its properties. W. C. W.

Hydrazinebenzenesulphonic Acids. By A. Pfülf (*Annalen*, **239**, 215—220).—Parahydrazinebenzenesulphonic acid readily unites with ketones, aldehydes, and thiocarbimides, but is not attacked by methyl iodide even in presence of alkalis. With nitrous acid, it yields diazobenzenesulphonic acid. *Acetonehydrazinebenzenesulphonic acid* crystallises in glistening plates which are sparingly soluble in hot water. It does not reduce alkaline solutions of copper sulphate. Hydrazinebenzenesulphonic acid dissolves in pyruvic acid, forming a syrupy liquid which slowly crystallises, and dissolves in alcohol and ether. The *sodium* salt, $C_9H_9N_2SO_5NNa + H_2O$, is deposited from hot dilute alcohol in colourless crystals. A warm solution of sodium hydrazinebenzenesulphonate dissolves benzaldehyde, forming the *sodium benzylidenehydrazinebenzenesulphonate*, which is deposited on the addition of alcohol. The *calcium* salt, $Ca(C_{13}H_{11}N_2SO_3)_2Ca + 4H_2O$, crystallises in needles. The free acid is decomposed by boiling water, or more easily by dilute acids, yielding benzaldehyde and hydrazinebenzenesulphonic acid. If phenyl thiocarbamide is substituted for benzaldehyde, a sulphonic acid is obtained which yields crystalline sodium and calcium salts, $(C_{13}N_3H_{12}S_2O_3)_2Ca + 2H_2O$.

Methylphenylhydrazine dissolves in strong sulphuric acid (to which 5 per cent. of sulphuric anhydride has been added), forming *methylhydrazinebenzenesulphonic acid*. The sulphonic acid crystallises in plates, dissolves in hot water, and forms condensation products with acetone, benzaldehyde, and pyruvic acid. The sodium and barium salts are soluble in water and sparingly soluble in alcohol.

W. C. W.

Anilides of Fumaric and Maleïc Acids: Phenylaspartic Acid. By R. Anschütz and Q. Wirtz (*Annalen*, **239**, 137—160).—*Fumaric dianilide*, $C_2H_2(CO{\cdot}NHPh)_2$, is obtained by carefully mixing ethereal solutions of fumaric chloride and aniline. It crystallises in white needles sparingly soluble in alcohol and glacial acetic acid, and decomposes at 275° without melting. It unites directly with two atoms of bromine, and seems to form the aniline of ordinary dibromosuccinic acid. The dianilide differs entirely from the fumaric dianilide which Michael and Wing (*Amer. Chem. J.*, **7**, 280) recently state they obtained together with "maleïc dianilide" by the distillation of monaniline malate. On repeating this experiment, the authors find that aniline malate is decomposed, yielding maleïnanil, phenylaspartanil, and fumaric dianilide, and that Michael and Wing mistook maleïnanil, $\ll^{CH{\cdot}CO}_{CH{\cdot}CO}>NPh$, for fumaric dianilide, and the anilide of phenylaspartic acid for maleïc dianilide. The yield of maleïnanil is increased if the operation is conducted under reduced pressure. *Maleïnanil* forms long yellow needles, freely soluble in benzene, chloroform, ether, and alcohol. It melts at 90—91°, and boils at 162·2° under 12 mm. pressure. (Under similar conditions citraconanil boils at 171·7°.) Maleïnanil unites with 2 atoms of bromine, forming *dibromosuccinanyl*, $C_4H_2Br_2O_2NPh$, a crystalline substance melting at 158—159°. On treatment with baryta-water at 30—40°, maleïnanil yields barium fumaranilate. *Fumaranilic acid*, $C_{10}H_9NO_3$, is deposited from alcohol in prisms melting at 187°. It is decomposed by alcoholic potash, forming fumaric acid. A solution of aniline acid maleate decomposes at the ordinary temperature, yielding a mixture of maleïc and phenylaspartic acids. The presence of the phenylmaleamic acid of Michel and Palmer (Abstr., 1886, 698) could not be detected. *Phenylaspartic acid*, $NHPh{\cdot}C_2H_3(COOH)_2$, is formed synthetically by boiling an aqueous solution of monobromosuccinic acid with aniline. The pure acid is a white crystalline substance which melts at 131—132° with decomposition, but it begins to change at 121°. The *barium* salt is freely soluble in water. The *hydrochloride*, $C_{20}H_{26}N_2O_{10},HCl$, forms monoclinic crystals [$a : b = 1{\cdot}9957 : 1$; $\beta = 75°\ 1\frac{1}{2}'$].

Phenylasparaginanil, $NHPh{\cdot}C_2H_3<^{CO}_{CO}>NPh$, is formed by boiling an aqueous solution of aniline maleate, and also by heating aniline with maleïc acid, aniline with maleïc anhydride, maleïnanil with aniline, and the aniline hydrogen malate. It forms a convenient starting point for the preparation of phenylaspartic acid. Its properties and its preparation from asparagine and aniline have been previously described by Piutti (*Gazzetta*, **14**, 474). W. C. W.

Sebaceodinitranilide. By G. Gehring (*Compt. rend.*, **104**, 1716—1717).—Diphenylsebacamide dissolved in fuming nitric acid or in a mixture of 4 parts concentrated sulphuric acid with 5 parts fuming nitric acid, yields a substance which has not yet been analysed, but which crystallises from water in white, feathery crystals melting at 133°.

Sebaceodinitranilide, $C_{10}H_{16}O_2(NH{\cdot}C_6H_4{\cdot}NO_2)_2$, crystallises from water in slender, white needles; from ether in needles, and often in somewhat large prisms with a square base. It melts at 116°, and can be sublimed. It has a very sweet taste, but does not reduce Fehling's solution. In order to prepare this compound, 2 grams of diphenylsebacamide is dissolved in 20 c.c. of nitric acid of sp. gr. 1·32, cooled, and mixed very slowly with 15 c.c. of nitric acid of sp. gr. 1·52 at 15°. The mixture is then heated in sealed tubes at 165° for six hours, and the product poured into water. The concentration of the nitric acid must be carefully regulated, since, if too strong, the diphenylsebacamide may be completely decomposed. The temperature and time of heating have much less influence on the result. C. H. B.

Metaformotoluide and its Derivatives. By S. Niementowski and M. Obremski (*Ber.*, **20**, 1891—1895). — *Metaformotoluide*, $C_6H_4Me{\cdot}NH{\cdot}COH$, boils with partial decomposition at about 278° (bar. 724 mm.), and is still liquid at −18°. Attempts to form a nitro-derivative were unsuccessful, the formic group being in all cases eliminated. *Methenylmetaditolylamidine*, $C_6H_4Me{\cdot}N:CH.NH{\cdot}C_6H_4Me$, is formed when formotoluide is maintained at the boiling point for some hours, carbonic anhydride being evolved. It crystallises in needles or scales, melts at 123°, and is soluble in benzene, ether, chloroform, and boiling alcohol. The *hydrochloride*, *platinochloride*, and *picrate* are all crystalline. *Dibromomethenylmetaditolylamidine*,

$$C_6H_4Me{\cdot}NBr{\cdot}CHBr{\cdot}NH{\cdot}C_6H_4Me,$$

formed by the action of bromine on a carbon bisulphide solution of the base, crystallises in white scales, sparingly soluble in chloroform and glacial acetic acid, insoluble in benzene; it blackens at 150°, and melts with decomposition at 262°. L. T. T.

Introduction of Carboxyl into Aromatic Derivatives by the Action of Diphenylcarbamide Chloride. By E. Lellmann and O. Bonhöffer (*Ber.*, **20**, 2118—2126. Compare this vol., p. 254).—*Diphenylparatoluylamide*, $C_6H_4Me{\cdot}CONPh_2$, is prepared by acting with diphenylcarbamide chloride on toluene in the presence of aluminium chloride. It crystallises in yellowish prisms, melts at 153—155°, is readily soluble in chloroform, benzene, and acetic acid, sparingly soluble in ether and light petroleum; and when heated with concentrated hydrochloric acid yields paratoluic acid. Under similar conditions, *xyloyldiphenylamide*, $C_6H_3Me_2{\cdot}CONPh_2$ [$CONPh_2$: Me : Me = 1 : 3 : 4], is obtained from orthoxylene. This crystallises in small, yellowish prisms, melts at 134—136°, shows a solubility similar to that of the preceding compound, and on hydrolysis yields paraxylic

acid (m. p. = 164—166°). *Xyloyldiphenylamide*, [$CONPh_2$: Me : Me 1 : 2 : 4] is obtained in like manner from metaxylene, and crystallises in yellowish monoclinic prisms, $a : b : c = 0{\cdot}9095 : 1 : ?$; $\beta = 83° 2'$; observed faces 0P, ∞P, $\infty\breve{P}\infty$, and a much curved hemidome. It melts at 141—142°, has a solubility similar to that of the foregoing compounds, and on hydrolysis yields xylic acid (m. p. = 126°).

Ortho-, meta-, and para-nitramines react with diphenylcarbamide chloride and yield nitrocarbamides. *Diphenylmetanitrophenylcarbamide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CONPh_2$, is formed by heating metanitraniline (2 mols.) with the chloride (1 mol.) at 120—125° for eight hours. It crystallises in very slender, bright yellow needles, melts at 154—155°, and is readily soluble in alcohol, benzene, chloroform, and acetic acid, sparingly soluble in ether and light petroleum. Under similar conditions, *diphenylparanitrophenylcarbamide* is prepared from paranitraniline, but the product has not been obtained free from a green colouring matter which is formed at the same time. It crystallises in pale bluish-green tables, melts at 175—176°, and is soluble in alcohol, &c., insoluble in ether and light petroleum. *Diphenylmetanitroparatolylcarbamide*, [Me : NO_2 : $NH{\cdot}CONPh_2$ = 1 : 3 : 4], is obtained in like manner from metanitroparatoluidine, and crystallises in small, yellow needles which melt at 138—139·5°, and are soluble in chloroform, benzene, &c. When it is heated in alcoholic solution with stannous chloride and concentrated hydrochloric acid for three hours in a reflux apparatus, *diphenylmetamidoparatolylcarbamide* is formed; this crystallises from alcohol in slender pale-coloured needles and melts at 135—137°; if, however, it is heated to 165—170° it becomes solid, and fuses a second time between 220° and 260°, decomposing into diphenylamine and toluylenecarbamide, melting at 299—301°; a compound probably identical with Sandmeyer's hydroxymethenyltoluylenediamine (this vol., p. 135).

Phenyl diphenylcarbamate, $Ph_2N{\cdot}COOPh$, is formed when equimolecular proportions of potassium phenate and diphenylcarbamide chloride in alcoholic solution are heated at 100°. It crystallises in short, pale-yellow prisms, melts at 103—104°, and is readily soluble in chloroform, alcohol, ether, benzene, and acetic acid. From potassium orthonitrophenate, under like conditions, *orthonitrophenyl diphenylcarbamate* is obtained; this compound separates at first in slender, yellow needles which soon aggregate to form colourless, monoclinic crystals having a diamond lustre, $a : b : c = 1{\cdot}8221 : 1 : 1{\cdot}6667$; $\beta = 82° 2'$; observed faces $\infty\breve{P}2$, P, $\infty\breve{P}\infty$, $-\breve{P}\infty$, 0P, $\frac{1}{2}\breve{P}\infty$, and $-$P. The needles melt at 114°, the prisms at 112°, and the salt dissolves in chloroform, benzene, &c. On reduction in alcoholic solution with stannous chloride and concentrated hydrochloric acid, it yields *orthamidophenyl diphenylcarbamate*, $Ph_2N{\cdot}COO{\cdot}C_6H_4{\cdot}NH_2$; this crystallises in slender, white needles, melts at 189—191°, dissolves readily in alcohol, benzene, and acetic acid, but sparingly in hot ether, and when heated at 190° for 8—10 hours yields diphenylamine and a compound crystallising in slender, white needles melting at 137—138°, most probably identical with Bender's anhydro-orthamidophenyl carbonate (this vol., pp. 38, 245; compare Abstr., 1883, 1169; this vol., pp. 135, 477). W. P. W.

Carbon Thiodichloride. By H. Bergreen (*Ber.*, **20**, 1965—1966).—By acting on water, ammonia, ammonium chloride, sodium ethoxide, sodium phenoxide, ethyl acetosodacetate, and ethyl sodiomalonate with carbon thiodichloride the following compounds were obtained: *tetraphenyl thiocarbamide*, $CS(NPh_2)_2$; *thiobenzophenone*, $CSPh_2$; *ethyl thiocarbonate*, $CS(OEt)_2$; *ethyl chlorothiocarbonate*, $CSCl{\cdot}OEt$; *phenyl thiocarbonate*, *ethyl thiocarboxylacetoacetate*, $CS:CAc{\cdot}COOEt$; and *ethyl thiocarboxylmalonate*, $CS:C(COOEt)_2$.

N. H. M.

Anhydro-compounds. By S. Niementowski (*Ber.*, **20**, 1874—1891).—The author's previous work on this subject (Abstr., 1886, 545) left the constitution of these compounds still somewhat in doubt. With the aim of settling this question, the author has examined the action of reducing agents on aromatic compounds of the formula

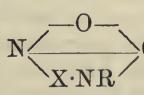
$$NO_2{\cdot}X{\cdot}NR{\cdot}CO{\cdot}C_xH_y\ [NO_2 : NR = 1 : 2],$$

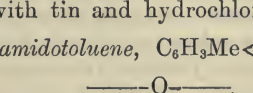
where the hydrogen of the acetylised nitrogen is replaced by an alkyl radicle. Such compounds on reduction should give rise to ortho-amido- or anhydro-compounds, $NH_2{\cdot}X{\cdot}NR{\cdot}CO{\cdot}C_xH_y$, or

$$X\!<\!\begin{matrix}-N\\ NR\end{matrix}\!>\!C{\cdot}C_xH_y.$$

If the latter were formed, it would show at once that in the condensation the oxygen-atom of the acid radicle removed the two hydrogen-atoms attached to the same nitrogen-atom. In the author's experiments, anhydro-compounds were formed, and he is therefore of opinion that the anhydro-compounds previously described are analogous in constitution and correspond with formula II given in that paper (*loc. cit.*).

But besides the anhydro-compounds the author obtained, during the reduction of the above-named substances, a new class of oxy-compounds to which he ascribes the formula



Metanitroparamethylacetotoluide, $NO_2{\cdot}C_6H_3Me{\cdot}NMe{\cdot}COMe$, was prepared by Gattermann's reaction (Abstr., 1875, 975). It crystallises in small plates, melts at 64°, and boils at 250—255° under 270 mm. pressure. When reduced with tin and hydrochloric acid, it yields a mixture of *methylethenyldiamidotoluene*, $C_6H_3Me\!<\!\begin{matrix}-N\\ NMe\end{matrix}\!>\!CMe$, and *oxymethylethenyldiamidotoluene*,  . The former crystallises in white needles, which are easily soluble in benzene, ether, &c., and in boiling water. It sublimes at 110°, forming thin cubic crystals, which melt at 142°; the melting point is lower when the substance is crystallised in the ordinary way. Its aqueous solution gives a reddish coloration when heated with ferric chloride. It dissolves in ammonia with blue fluorescence. Concentrated hydrochloric acid does not decompose it even at 250°. The *hydrochloride* crystal-

lises with $\frac{1}{2}$ mol. H_2O in needles, the *platinochloride* in yellow rhombic plates, melting with decomposition at 234—244°.

The oxy-compound crystallises in long needles containing $2H_2O$, which is given off at 100°. It is soluble in boiling water, alcohol, and chloroform, sparingly so in boiling benzene and ether. The anhydrous substance melts at 63°. It is not decomposed by concentrated hydrochloric acid even at 180°, nor by boiling alcoholic potash, nor is it reduced by long-continued boiling with tin and hydrochloric acid. The *hydrochloride* forms white, glistening needles soluble in water; the *platinochloride*, yellow scales melting with decomposition at 220°. When heated, this oxy-compound melts to a clear liquid, and at a slightly higher temperature explodes, leaving a thick brownish liquid, and a small quantity of methylethenyldiamidotoluene. When heated with zinc-dust or with soda-lime, the decomposition takes place more quietly, methylethenyldiamidotoluene being the chief product. Boiling acetic anhydride appears to act in a similar way, an aceto-derivative of the non-oxygenated base being formed. Concentrated sulphuric acid has no action on the oxy-compound at 100°.

Metanitroparethylacetotoluide resembles the methyl-compound, and volatilises with difficulty in a current of steam. Ethylethenyldiamidotoluene (monethylanhydracetodiamidotoluene) has been already described by Hübner, Kronberg, and Tubbe (Abstr., 1882, 505). The *hydrochloride* forms a gummy mass; the *mercurochloride* crystallises in needles; the *picrate* forms crystals sparingly soluble in alcohol. The oxy-compound was not isolated, and if formed at all was only produced in very small quantities. When ethenyldiamidotoluene is heated with methyl iodide and methyl alcohol, it yields *methylethenyldiamidotoluene methiodide*, soluble in alcohol and water, crystallising in needles, and melting at 221°. When heated with strong potash, the methiodide yields the corresponding *hydroxymethide*. This ammonium base crystallises in thin scales which soften at 115° and melt at 135°. It is a strong base, is insoluble in alkalis, and is not decomposed by heating with concentrated hydrochloric acid. The *hydrochloride*, *platinochloride*, and *picrate* are all crystalline. From the stability of the base, the author is inclined to consider its formula to be $C_6H_3Me<^{NMe}_{NMe}>CMe\cdot OH$.

Tetramethyldiamidotoluene, $C_6H_3Me(NMe_2)_2$ [Me : NMe_2 : NMe_2 = 1 : 3 : 4], is formed when toluylenediamine is heated in closed tubes at 120—130°. It is a colourless, mobile liquid of strongly basic odour. It boils at 225·5° (uncorr.) under 717 mm. pressure. It is easily miscible with the usual solvents, sparingly soluble in water. The *platinochloride*, *picrate*, and *mercurochloride* are crystalline. *Nitrotetramethyldiamidotoluene*, formed by the action of nitrous acid on the base, crystallises in hexagonal prisms, is easily soluble in alcohol, ether, and benzene, and melts at 63°. It is still basic in properties. It is soluble in phenol, but sulphuric acid added to this solution only causes a slight lilac coloration, showing that no nitroso-group is present.

L. T. T.

Nitrosalicylaldehydes. By W. v. Miller (*Ber.*, **20**, 1927—1931). Mazzara has (this Journal, 1877, i, 597) described an α- and a β-nitro-

salicaldehyde. The α-aldehyde (true m. p. 109°) when oxidised in acetic solution with chromic acid gives 1 : 2 : 3 nitrosalicylic acid, and is therefore 1 : 2 : 3 *nitrosalicaldehyde*, [COH : OH : NO_2 = 1 : 2 : 3]. The β-aldehyde (true m. p. 126°) when similarly treated gives 1 : 2 : 5 nitrosalicylic acid, and is therefore 1 : 2 : 5 *nitrosalicylaldehyde*. L. T. T.

Nitrocoumaraldehydes. By W. v. Miller and F. Kinkelin (*Ber.*, **20**, 1931—1934).—Tiemann and Kees described (Abstr., 1885, 1073) orthocoumaraldehyde, but were unable to obtain it by the condensation of salicylic and acetic aldehydes. The authors find that the introduction of a nitro-group into salicaldehyde renders the condensation possible.

1 : 2 : 5 *Nitrocoumaraldehyde*, [C_2H_2·COH : OH : NO_2 = 1 : 2 : 5], was obtained by dissolving 100 grams of the sodium salt of 1 : 2 : 5 nitrosalicylaldehyde (preceding Abstract) in $2\frac{1}{2}$ litres of water, and adding 60 grams acetaldehyde, and 150 grams of 10 per cent. alcoholic potash. It is soluble in alcohol and acetic acid, very sparingly so in boiling water; it crystallises in yellow needles, and melts with decomposition at 200°. The *phenylhydrazide* crystallises in orange scales melting at 235°; the *sodium-derivative* forms red plates easily soluble in water.

1 : 2 : 3 *Nitrocoumaraldehyde*, from 1 : 2 : 3 nitrosalicaldehyde, crystallises in glistening yellow needles, melts at 133°, and is easily soluble in alcohol and acetic acid, sparingly so in ether and boiling water. Its *phenylhydrazide* crystallises in red scales, and melts at 157°. L. T. T.

Nitrosalicylaldehyde and Nitrocoumarin. By C. Taege (*Ber.*, **20**, 2109—2110).—A summary of the author's inaugural dissertation, which was published previously to the appearance of v. Miller's paper (preceding Abstract). Salicylaldehyde, when nitrated either with fuming nitric acid in a freezing mixture, or by boiling with dilute nitric acid, yields nitrosalicylic acid and two isomeric nitrosalicylaldehydes. The latter can be separated by means of their barium-derivatives, since on treatment with barium hydroxide the aldehyde melting at 107° crystallises first in orange crystals with 2 mols. H_2O, and that melting at 125° forms yellow spangles with 3 or 6 mols. H_2O, and separates from the second crystallisation. The sodium hydrogen sulphite compound of the former does not crystallise, that of the latter is solid, whilst the phenylhydrazides melt at 165° and 186° respectively.

The *nitrocoumarin* obtained by direct nitration with fuming nitric acid melts at 183°, and the corresponding *amido*-derivative formed by reduction with ferrous sulphate melts at 161°; on oxidation with potassium permanganate in alkaline solution, it yields nitrosalicylic acid, [COOH : OH : NO_2 = 1 : 2 : 5] (m. p. = 228°). A *dibromonitrocoumarin*, melting at 271°, is formed by the prolonged action of bromine-vapour.

When nitrosalicylaldehyde (m. p. 125°) is boiled with acetic anhydride and sodium acetate, nitrocoumarin melting at 183° and iden-

tical with the preceding derivative is obtained; if, however, a lower temperature is employed in the reaction, an acetyl-derivative of nitrosalicylaldehyde results; this melts at 112°, and loses its acetyl-group on boiling with water. Under similar conditions, nitrosalicylaldehyde (m. p. = 107°) yields a compound, probably a nitrocoumarin, from which a nitrosalicylic acid (m. p. = 145°) was obtained on oxidation, and at a lower temperature forms an acetyl-derivative; this melts at 110°, and is also decomposed into nitrosalicylaldehyde on boiling with water. W. P. W.

Isophthaldehyde. By V. Meyer (*Ber.*, **20**, 2005).—Isophthaldehyde, $C_8H_6O_2$, crystallises in long needles melting at 89—90°, has a very slightly aromatic odour, and reduces silver solution with difficulty; it can be distilled in small quantities without decomposition. The oxime crystallises from hot water in needles, which melt at 180°. When the latter is left in contact with twice its weight of acetic chloride for 12 hours, dicyanobenzene is formed (compare this vol., p. 482). N. H. M.

Benzoylaldehyde. By L. Claisen and L. Fischer (*Ber.*, **20**, 2191—2193).—*Benzoylaldehyde*, $CH_2Bz{\cdot}COH$, is obtained as a sodium-compound when a mixture of acetophenone and ethyl formate in molecular proportions is added to a dilute alcoholic solution of sodium ethoxide (1 mol.) cooled in ice, and separates as a colourless or pale-yellow oil, on treatment of the aqueous solution of the salt with acetic acid. Its alcoholic solution gives an intense red coloration with ferric chloride. The *copper* salt, $(C_9H_7O_2)_2Cu$, crystallises in dark-green, glistening, flat prisms. On adding a solution of a salt of the corresponding base to the aqueous solution of the sodium compound of benzoylaldehyde, the following derivatives are obtained: the *anilide*, $CH_2Bz{\cdot}CH : NPh$, crystallising in short, prismatic or scaly yellow forms melting at 140—141°; the *paratoluidide*, $CH_2Bz{\cdot}CH : NC_7H_7$, crystallising in small, yellow forms melting at 160—163°, and the *β-naphthalide*, $CH_2Bz{\cdot}CH : NC_{10}H_7$, crystallising in small, bronze-coloured forms, melting at 180—182°. The anilide could not be converted into a quinoline-derivative either by heating alone or with concentrated sulphuric acid, and on dry distillation passes over for the most part unchanged. W. P. W.

Aromatic Ketones. By K. Elbs (*J. pr. Chem.* [2], **35**, 465—509; compare Abstr., 1886, 461).—Ditolyl ketone is prepared as follows: 50 grams of aluminium chloride, 60—70 c.c. of toluene, and 50 c.c. of carbon bisulphide are put into a strong half-litre flask; 10—12 c.c. of carbon bisulphide saturated with carbon oxychloride is added, and the flask closed with a cork provided with a glass tap drawn out to a fine capillary, which is fastened with wire. The whole is slightly warmed with steam for 15 to 30 minutes, allowed to cool, and the pressure relieved. It is then treated with more carbon oxychloride as before; this is repeated three or four times, and the product treated as previously described (*loc. cit.*). The yield is 40 to 50 per cent. of the theoretical.

Orthoxylyl phenyl ketone, $C_6H_3Me_2 \cdot COPh$ [Me : Me = 1 : 2], prepared from benzoic chloride and orthoxylene, crystallises from alcohol in groups of white, matted needles; it melts at 47—48°, boils at 340·2° under 744 mm. pressure, and is readily soluble in the usual solvents, except water.

Orthoxylyl phenyl carbinol, $C_6H_3Me_2 \cdot CHPh \cdot OH$, is readily obtained by reducing the ketone with zinc-dust and potash. It crystallises in groups of white needles, which dissolve readily in the usual solvents, except water; it melts at 68°, and boils at 336° under 744 mm. pressure with slow decomposition.

Metaxylyl phenyl ketone, forms a rather thick colourless oil boiling at 321·2° under 744 mm. presence. In solubility, it resembles the ortho-compound. When boiled for 12 hours, a small amount of β-methylanthraquinone melting at 170—172° is formed; when the ketone is boiled in presence of metaxylyl carbinol, β-methylanthracene is obtained.

Metaxylyl phenyl carbinol, $C_{15}H_{16}O$, is best purified by distillation. It melts at 57° and boils at 330·8°, under 744 mm. pressure.

Paraxylyl phenyl ketone, [Me : CO : Me = 1 : 2 : 4], separates from its alcoholic solution in large, clear, well-formed prisms, very readily soluble in ether, alcohol, and acetone, sparingly in glacial acetic acid, more soluble in benzene; it melts at 36°, and boils at 317·2° under 744 mm. pressure. When boiled, it yields methylanthracene melting at 199—200°. The *disulphonic acid* is obtained by dissolving the ketone in pyrosulphuric acid; the *barium salt*, a yellow crystalline substance, is readily soluble in water. When the ketone is heated with nitric acid (sp. gr. 1·15) at 170° to 180° for six hours, it is oxidised to benzoylterephthalic acid.

Paraxylyl phenyl carbinol crystallises in prisms which melt at 88°, dissolve very sparingly in water, readily in alcohol, ether, acetone, and benzene.

Diparaxlyl phenyl methane, $CHPh(C_6H_3Me_2)_2$, is prepared by Hemilian's method (this Journ., 1875, 152, and *Ber.*, **16**, 2360); it crystallises from light petroleum in colourless prisms which melt at 92·5°, boils above 360°, and dissolves in the usual solvents except water. The solutions show a blue fluorescence.

Dixylyl phenyl β-pinacoline, $CPhBz(C_6H_3Me_2)_2$, is obtained by Thömer and Zincke's method (*Ber.*, **11**, 65 and 1396). It forms almost colourless prisms, rather readily soluble in alcohol, ether, benzene, and light petroleum; it melts at 146°. When heated with soda-lime, diparaxylyl phenyl ketone is formed.

Diparaxylyl ketone, $CO(C_6H_3Me_2)_2$ [CO : Me_2 = 2 : 1 : 4 and 5 : 1 : 4], is prepared in a manner similar to diparaxlylyl ketone. It is a thick, pale-yellow liquid, boiling at 325—327° (uncorr.). When boiled, it gives up the elements of water, and is converted into *trimethyl-anthracene*, $C_6H_2Me_2$ C_6H_3Me [Me_2 = 1 : 4 and Me = 2]. The latter crystallises in colourless plates, which show a blue fluorescence and melt at 227°. It sublimes below 100°, dissolves readily in ether and benzene, very sparingly in cold alcohol.

Diparaxylyl carbinol, $CH(C_6H_3Me_2)_2 \cdot OH$, crystallises from alcohol in white needles melting at 131°. In solubility, it resembles its homologue.

Triparaxlylmethane, $CH(C_6H_3Me_2)_3$, is prepared by boiling a solution of diparaxylyl carbinol in paraxylene with phosphoric anhydride in a reflux apparatus for four hours. It crystallises from alcohol in colourless crystals which melt at 188°, and are moderately soluble in alcohol, readily in ether and benzene. It boils above 360°.

Mesityl phenyl ketone (Louïse, Abstr., 1883, 577; 1884, 905) is best prepared by the general method previously described (*loc. cit.*); an excess of mesitylene need not be used. It melts at 35° and boils at 318—319°; no anthracene-derivative could be obtained from it. The carbinol (Louïse, *loc. cit.*) is best prepared by reducing the ketone with zinc-dust and potash. When the ketone is heated with strong sulphuric acid in a water-bath, mesitylenesulphonic acid and benzoic acid are formed; when the temperature does not rise above 50°, *mesitylphenylketonesulphonic acid* is formed; the *barium salt* is a yellow powder. When 2 grams of the ketone is dissolved in 30 c.c. of nitric acid (sp. gr. 1·45) and 10 c.c. of pyrosulphuric acid, two isomeric *trinitro-compounds* are formed; the one crystallises in slender, colourless needles which melt at 188°, almost insoluble in alcohol; the other crystallises from alcohol, in which it is rather readily soluble, in colourless needles melting at 145°. Nitric acid (sp. gr. 1·1) at 200° converts the ketone into a mixture of acids from which *benzoyl uvitic acid*, $COPh \cdot C_6H_2Me \cdot COOH$ [Me : CO : $(COOH)_2$ = 1 : 2 : 3 : 5 or 5 : 2 : 1 : 3], was isolated; this crystallises from hot water in slender white needles melting at 245°.

Pseudocumyl phenyl ketone, $COPh \cdot C_6H_2Me_3$, boils at 328—329°; when boiled, no dimethylanthracene but dimethylanthraquinone is formed; sulphuric acid converts it into benzoic and pseudocumenesulphonic acids. When nitrated, two isomeric *trinitropseudocumyl phenyl ketones* are obtained; both crystallise in slender needles; the one is sparingly soluble and melts at 185°, the other which is rather readily soluble melts at 155°. When oxidised with dilute nitric acid, *benzoyltrimellitic acid*, $C_6H_2Bz(COOH)_3$ [Bz : $(COOH)_3$ = 5 : 1 : 2 : 4] is formed together with other products.

Paracymyl phenyl ketone (Kollarits and Merz, *Ber.*, **6**, 546 and 1264), prepared in a manner similar to the other ketones, is a readily soluble thick oil boiling at 175°. When boiled for eight days, a small amount of ordinary anthracene is formed.

Paracymyl phenyl carbinol forms a thick, pale-yellow oil.

Paraxylylparacymylphenylmethane, $C_6H_3Me_2 \cdot CHPh \cdot C_6H_3MePr$, is prepared by adding 20 grams of phosphoric anhydride to a solution of 30 grams of paracyml phenyl carbinol in 30 grams of paraxylene, and boiling the whole for five hours. It is a thick, reddish-yellow oil which boils above 360°.

Dinitroparacymyl phenyl ketone, $C_{17}H_{16}O(NO_2)_2$, is obtained by adding potassium nitrate to a solution of the ketone dissolved in 10 parts of sulphuric acid; it forms white flakes rather readily soluble in ether, acetone, and benzene, &c., and could not be crystallised.

When the ketone is heated with nitric acid (sp. gr. = 1·1) at 250° benzoylterephthalic acid is formed. The *sulphonic acid* of the ketone is obtained by the action of pyrosulphuric acid at 60°; the *barium salt* is a yellow powder.

α-Naphthyl phenyl ketone, $COPh{\cdot}C_{10}H_7$ (Kollarits and Merz, *Ber.*, **13**, 360), is prepared from naphthalene and benzoic chloride. *α-Naphthylphenyl-β-pinacoline*, $C_{34}H_{24}O$, is a greenish-yellow substance which melts at 130°; it is readily soluble in acetone and ether.

Di-α-naphthyl phenyl carbinol, $CPh(C_{10}H_7)_2{\cdot}OH$, is obtained together with benzaldehyde by boiling the β-pinacoline with alcoholic potash; it is a crystalline substance, readily soluble in ether and acetone, less soluble in alcohol and benzene, and melts at 160° to 170°. When distilled with two or three parts of zinc-dust, α-naphthylphenylmethane (m. p. 58·5°) and *dinaphthylphenylmethane* are formed. The latter resembles the carbinol in solubility and melts at about 180°. It is best prepared by distilling the β-pinacoline with zinc-dust. *Dinitromonobromo-α-naphthyl phenyl ketone*, $C_{17}H_9OBr(NO_2)_2$, is obtained by dissolving as much of the bromo-ketone as possible in 10 c.c. of nitric acid (sp. gr. 1·48); it crystallises from a mixture of ether and alcohol in small, lustrous, deep-yellow crystals which melt with evolution of gas at 90°. N. H. M.

Introduction of Acid Radicles into Ketones. By C. Beyer and L. Claisen (*Ber.*, **20**, 2178—2188).—Acetylacetophenone is obtained by adding acetophenone (1 mol.) to a mixture of sodium ethoxide free from alcohol (1 mol.) and ethyl acetate (2 mols.), cooled in ice, and subsequently decomposing the sodium-compound (which separates in slender, bright yellow crystals) with acetic acid; the yield amounts to 80—90 per cent. of the acetophenone employed, and the product is identical with benzoylacetone prepared in like manner from acetone and ethyl benzoate, and with that obtained from ethyl benzoylacetoacetate (Abstract, 1885, 1237). The amido- or imido-derivative, $C_{10}H_{10}O:NH$, forms colourless, glistening rhombic crystals; $a : b : c = 0{\cdot}99275 : 1 : 0{\cdot}88205$; and the *copper*-derivative, $(C_{10}H_9O_2)_2Cu$, crystallises from benzene or alcohol in bright green needles. By employing the corresponding homologues of ethyl acetate in the above reaction, the following derivatives have been prepared: *propionylacetophenone*, sp. gr. = 1·081 at 15°, boiling point = 276—277° at the ordinary, and = 170—172° at 30—31 mm. pressure; *butyrylacetophenone*, sp. gr. = 1·061 at 15°, boiling point = 174° at 24 mm. pressure; *isobutyrylacetophenone*, boiling point = 170° at 26 mm. pressure; *valerylacetophenone*, boiling point = 183—184° at 30 mm. pressure.

Ethyl benzoylpyruvate, $CH_2Bz{\cdot}CO{\cdot}COOEt$, is obtained by dissolving 9·2 grams of sodium in 150 grams of alcohol, adding to the solution cooled in ice 48 grams of acetophenone and 58·4 grams of ethyl oxalate, and decomposing the crystalline sodium salt in aqueous solution by a current of carbonic anhydride; the yield amounts to 78 per cent. of that theoretically possible. It crystallises in long prisms, is readily soluble in the ordinary solvents, and yields a *copper* salt, $(C_{12}H_{11}O_4)_2Cu$, crystallising from benzene or alcohol in long, slender needles. The

ethyl salt, when heated with dilute aqueous soda, yields acetophenone, ethyl alcohol, and sodium oxalate, and on treatment with alcoholic ammonia in the cold is converted into acetophenone, ethyl alcohol, and oxamide. The *acid* is formed, together with a small quantity of a compound (oxalyldiacetophenone ?) crystallising in yellow, benzil-like needles melting at 179°, when 2 mol. props. of acetophenone are employed in the foregoing reaction. It crystallises in yellowish-white prisms, melts at 155—156°, is soluble in alkalis, and alkaline carbonates and acetates, and evolves carbonic anhydride when heated above its melting point.

Ethyl diphenylpyrazolecarboxylate, $C_3NHPh(NPh)\cdot COOEt$, is formed when 10 grams of phenylhydrazine are added to 20 grams of ethyl benzoylpyruvate dissolved in 100 grams of acetic acid and the mixture boiled for two hours in a reflux apparatus. It crystallises in compact prisms, melts at 90°, is readily soluble in methyl and ethyl alcohol, ether, and chloroform, and distils at about 400° with partial decomposition. On saponification with concentrated aqueous soda and treatment in the cold with hydrochloric acid, *diphenylpyrazolecarboxylic acid* is obtained; this crystallises from alcohol in glistening forms of the composition $C_{16}H_{12}N_2O_2 + EtOH$, melts at 185°, and is readily soluble in acetone, chloroform, and acetic acid, soluble in methyl alcohol and benzene, very sparingly soluble in water. When heated to 250°, the acid evolves carbonic anhydride and is converted into *diphenylpyrazole;* this is a thick pale-yellow oil which boils at 335—336°, and on the addition of a particle of its crystalline hydrochloride solidifies to a silky, brittle mass melting at 56°.

The introduction of the acid radicle of an ethereal salt into a second ethereal salt or into a ketone by the action of sodium ethoxide, is regarded as due not to the direct withdrawal of the elements of ethyl alcohol by the ethoxide, but to the formation of an unstable double compound of the ethereal salt and sodium ethoxide, $R\cdot C(ONa)(OEt)_2$, which on the addition of the second ethereal salt or ketone undergoes decomposition as expressed by the equation $R\cdot C(ONa)(OEt)_2 + CH_3\cdot COOEt = R\cdot C(ONa) : CH\cdot COOEt + 2EtOH$. The fact that dilute alcoholic solutions of sodium ethoxide can be employed in these synthetical reactions in place of the pure compound affords evidence in favour of this view. W. P. W.

Nitrosoketones. By L. Claisen and O. Manasse (*Ber.*, **20**, 2194—2198).—Nitrosoacetophenone (this vol., p. 575) crystallises from a chloroform solution, by slow evaporation, in colourless or pale-yellow, glistening, monoclinic prisms, $a : b : c = 2\cdot762 : 1 : 2\cdot146$; $\beta = 66° 54'$; observed faces, 0P, $\infty P\infty$, ∞P, $+P\infty$, $+2P\infty$, and a hemipyramid probably $-P$. The dry sodium salt decomposes very readily and explodes in a warm place or on contact with a trace of sulphuric acid, nitric acid, bromine, &c., with the formation of hydrogen cyanide and sodium benzoate; a similar decomposition is also effected by boiling the salt with dilute aqueous soda. When distilled, the ketone yields a mixture of hydrocyanic acid, benzoic acid, and benzoyl cyanide, and inasmuch as the compounds formed when it is treated with acetic anhydride and acetyl chloride give benzoyl

cyanide on distillation, it is probable that this is the first product of the change, and that it subsequently undergoes decomposition into hydrogen cyanide and benzoic acid. Nitrosoacetone when similarly treated also gives a good yield of acetyl cyanide. The readiness with which the nitroso-ketones undergo conversion into acid cyanides renders it evident that the colour reactions they give with sulphuric acid and benzene containing thiophen (Abstr., 1880, 67) and with sulphuric acid and phenol (Abstr., 1878, 659; this vol., p. 575) are due not to the ketones but to the cyanides formed by their decomposition, and this view is confirmed by the fact that benzoyl cyanide and acetyl cyanide yield with sulphuric acid and phenol colours identical in shade and intensity with those given by the corresponding nitroso-ketones. When an aqueous solution of the sodium salt of nitrosoacetophenone is treated with sulphurous anhydride, a compound, $C_8H_{11}O_5NS$, is obtained, which crystallises in white prisms or small needles, is sparingly soluble in water, and shows all the properties of a strong acid.

Benzoyl cyanide can readily be prepared, without the previous separation of nitrosoacetophenone, by gradually adding amyl nitrite (1 mol.) to a mixture of acetophenone (1 mol.) and acetyl chloride (3 mols.) heated at 100°, and distilling the product; the yield amounts to 65—70° per cent. of that theoretically possible. W. P. W.

Derivatives of Orthotoluic Acid. By S. Racine (*Annalen*, **239**, 71—78).—Orthotoluic acid is conveniently prepared by heating in a flask provided with a reflux condenser a mixture of phthalide, hydriodic acid (b. p. 127°), and phosphorus. The crude acid is dissolved in sodium carbonate. The sodium salt, $C_7H_7{\cdot}COONa + 2H_2O$, forms glistening plates which effloresce and become anhydrous. The anhydride, $(C_6H_4MeCO)_2O$, is formed by the action of phosphorus oxychloride on the anhydrous sodium salt. It melts at 36—38° and boils at 325°. It is soluble in ether and benzene, and is slowly attacked by hot water.

Bromorthotoluic acid (m. p. 167°) yields on oxidation with dilute nitric acid bromophthalic acid (m. p. 156—158°). The anhydride of this bromophthalic acid melts at 95°.

A small quantity of bromophthalide is formed by the action of bromine on orthotoluic acid at 130°. It is soluble in alcohol and ether and melts at 98—100°. When oxidised, it yields α-bromophthalic acid.

Methyldinitrorthotoluate is deposited from alcohol in colourless needles and melts at 73—74°. Dinitro-orthotoluic acid is converted by oxidation with dilute nitric acid into the dinitrophthalic acid melting at 226°, which Beilstein and Kurbatoff obtained from β-dinitronaphthalene. W. C. W.

Chlorosalicylic Acids. By L. Varnholt (*J. pr. Chem.* [2], **36**, 16—31).—Chlorosalicylic acid [COOH : OH : Cl = 1 : 2 : 5] is obtained by filling an autoclave with pure, dry sodium parachlorophenoxide and connecting it with a vessel containing liquid carbonic anhydride. The absorption of carbonic anhydride takes place with

considerable rise of temperature; after half an hour, the autoclave is heated for three to four hours at 140—150°. The product is an almost white powder.

An *isomeride* of the above acid having the constitution

$$[COOH : OH : Cl = 1 : 2 : 3],$$

is prepared from sodium orthochlorophenol. It crystallises in long needles melting at 178°, distils with steam, and sublimes with slight decomposition; it dissolves sparingly in water, readily in alcohol, chloroform, and glacial acetic acid, and gives an intense violet colour with ferric chloride. The *sodium salt* crystallises in plates, very readily soluble; the *barium salt* (with 3 mols. H_2O) forms white needles readily soluble in alcohol, less soluble in water. The *silver* and *lead salts* are white, insoluble substances. The *methyl salt* crystallises from alcohol in needles melting at 83°; it boils at 259—260° with partial decomposition.

Chlorosalicylic acid [COOH : OH : Cl = 1 : 2 : 4], prepared from sodium metachlorophenoxide, crystallises from water in small needles melting at 207°; it dissolves very readily in alcohol, benzene, chloroform, and glacial acetic acid, sparingly in water; it distils with steam, sublimes with slight decomposition, and gives an intense violet colour with ferric chloride. The acid was also prepared from nitrochlorotoluene [Me : NO_2 : Cl = 1 : 2 : 4] by oxidising it with nitric acid (sp. gr. 1·1) at 185° to nitrochlorobenzoic acid; this is then reduced, and the amido-acid diazotised. The *nitrochlorobenzoic acid* [COOH : NO_2 : Cl = 1 : 2 : 4], obtained as intermediate product, crystallises in long needles melting at 138—139°.

Metachlorophenol is prepared as follows:—Chlorine is passed into 500 grams of nitrobenzene containing 10 grams of ferric chloride until the whole weighs 650 grams. It is purified by distillation, and reduced with tin and hydrochloric acid to metachloraniline; 10 grams of the latter is dissolved in 2 litres of water, treated with the calculated amount of sulphuric acid, cooled, and sodium nitrite added. After some time, it is heated on a water-bath; it is then extracted with ether and the metachlorophenol purified by distillation.

N. H. M.

Action of Phosphorous Chloride on Salicylic Acid and Phenol. By R. Anschütz and W. Emery (*Annalen*, **239**, 301—313). —Phosphorus trichloride acts on salicylic acid at 70°, forming the compound $C_7H_4O_3PCl$, according to the equation $OH{\cdot}C_6H_4{\cdot}COOH + PCl_3 = C_7H_4O_3PCl + 2HCl$. The authors regard the new substance as the monochloride of salicylophosphorous acid, $C_6H_4<^{CO\cdot O}_{\ \ O\ -}>PCl$. The chloride melts at 36—37°, and boils at 127° under 11 mm. pressure. It is soluble in alcohol, ether, and chloroform, and is decomposed by water into salicylic and phosphorous acids. Phosphoric chloride converts this substance into the compound $C_7H_4O_3PCl_3$. The new chloride is either identical with or closely resembles the product of the action of phosphoric chloride on salicylic acid.

The former boils at 167° under 11 mm. pressure, the latter at 168°. The sp. gr. of the substances are 1·55702 and 1·56207 respectively.

The chloride of salicylophosphorous acid unites directly with 2 atoms of bromine, forming a strongly refractive liquid, $C_7H_4ClBr_2PO_3$, which boils at 185—138° under 12 mm. pressure.

Noack (Abstr., 1883, 737) has shown that phenyl phosphoryldichloride, $PhOPCl_2$, diphenyl phosphoryldichloride, Ph_2O_2PCl, and triphenyl phosphite, Ph_3PO_3, are formed by the action of phosphorous chloride on phenol. They may be separated by distillation under reduced pressure, as they boil at 90°, 172°, and 220° respectively under 11 mm. pressure.

Phenyl phosphoryldichloride is converted into the compound $PhOPCl_4$, by the action of phosphorus penatchloride. W. C. W.

Action of Phosphoric Chloride on Salicylic Acid. By R. Anschütz and G. D. Moore (*Annalen*, **239**, 314—333).—The compound $C_7H_4Cl_3PO_3$, which is formed by the action of phosphorus pentachloride (1⅓ mols.) on dry salicylic acid (1 mol.) (Abstr., 1885, 1061), is converted into the chloride $C_7H_4Cl_5PO_2$, by the action of a second molecule of phosphoric chloride at 170°. On distillation under 11 mm. pressure, the new compound is obtained as a colourless liquid boiling at 178—179°; sp. gr. = 1·62019 at 20° compared with water at 4°. It is decomposed by water, yielding phosphoric and salicylic acids, and is converted into orthobenzoyl trichloride by the action of a third molecule of phosphoric chloride at 180°.

The chloride, $C_7H_4Cl_3PO_3$, is decomposed by slow distillation under the ordinary atmospheric pressure, yielding phosphorus oxychloride, orthochlorobenzochloride, orthochlorobenzotrichloride, and the compound $C_7H_4ClPO_4$. W. C. W.

Action of Phosphoric Chloride on Meta- and Para-hydroxybenzoic Acids. By R. Anschütz and G. D. Moore (*Annalen*, **239**, 333 — 349). — *Metachlorocarbonylphenylphosphoric dichloride*, $COCl\cdot C_6H_4\cdot O\cdot POCl_2$ [1 : 3], is formed by the action of phosphoric chloride (1⅓ mols.) on metahydroxybenzoic acid (1 mol.). It boils at 168—170° under 11 mm. pressure, and is partially decomposed by distillation under atmospheric pressure. Its sp. gr. at 20° is 1·54844. It dissolves slowly in water, and the concentrated solution deposits crystals of *metacarboxylphenylorthophosphoric acid*,

$$COOH\cdot C_6H_4\cdot O\cdot PO(OH)_2.$$

The acid melts at 200—201°, and dissolves in water, alcohol, and ether. The aqueous solution is decomposed at 150°.

By the action of phosphoric chloride at 150°, the compound $C_7H_4Cl_3PO_3$ is converted into $C_7H_4Cl_5PO_2$, probably $COCl\cdot C_6H_4\cdot O\cdot PCl_4$. This substance boils at 176—179° under 11 mm. pressure. It is decomposed by water, yielding metacarboxylphenylphosphoric acid, and is converted into metachlorobenzotrichloride by the action of phosphoric chloride at 180°.

The following are the products of the action of 1 and 2 mols. of phosphoric chloride on anhydrous parahydroxybenzoic acid:—1. *Parachlorocarbonylphenylorthophosphoric dichloride*, and 2, parachlorobenzoyl chloride. The chloride, $C_7H_4Cl_3PO_3$, is a refractive liquid boiling at

176° under 13 mm. pressure, and partly decomposed by distillation under the ordinary pressure. It is converted into paracarboxylphenylphosphoric acid by the action of water. W. C. W.

Preparation of Mandelic Acid by its Derivatives. By C. Engler and E. Wöhrle (*Ber.*, **20**, 2201—2204).—When dibromacetophenone is treated with dilute aqueous potash, it is converted into mandelic acid according to the equation $COPh{\cdot}CHBr_2 + 2KOH = OH{\cdot}CHPh{\cdot}COOH + 2KBr$, the dihydroxyacetophenone,

$$COPh{\cdot}CH(OH)_2,$$

whose formation might be first expected, evidently being too unstable to exist, and so suffers change into the isomeric mandelic acid. Metanitromandelic acid was prepared in like manner from metanitracetophenone dibromide.

Orthonitromandelic acid, $NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}COOH$, prepared from orthonitracetophenone dibromide, forms small crystals, melts at 140°, but decomposes at a little above 100° when slowly heated. It dissolves readily in water, alcohol, ether, and chloroform. When reduced with tin and hydrochloric acid, it is converted into the hydrochloride of the corresponding amido-acid; this forms a crystalline mass, but owing to its instability could not be obtained in a pure state. There is little doubt that the product of its decomposition is dioxindole, $C_6H_4<\begin{matrix}CH(OH)\\ -NH-\end{matrix}>CO$. A. J. G.

Reduction of Orthonitrophenylglycollic Acid. By L. Duparc (*Ber.*, **20**, 1942—1945).—The author has examined the compound $C_8H_7NO_2$, which Fritsche obtained by the reduction of the above acid (Abstr., 1880, 320) in order to determine whether its constitution is $C_6H_4<\begin{matrix}-O{\cdot}CH_2-\\ NH{\cdot}CO\end{matrix}>$ or $C_6H_4<\begin{matrix}-O{\cdot}CH_2-\\ N:C(OH)\end{matrix}>$. This substance appears to be isomeric with that lately obtained by Aschan (this vol., p. 814) by the action of potash on chloracetoamidophenol, and to which that investigator has ascribed the first of the above formulæ.

Acetic anhydride had no action on the compound even at 180°. Attempts to replace one of the oxygen-atoms by the imide group proved unsuccessful. When heated with zinc-dust, a very small quantity of a base, C_8H_9NO, boiling at about 200°, was obtained. *Ethyl orthonitrophenylglycollate*, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}COOEt$, forms colourless needles melting at 49°, and soluble in alcohol, ether, and benzene, insoluble in water. When reduced with tin and hydrochloric acid, the ethyl group is eliminated, and a *base*, $C_8H_6ClNO_2$, formed which appears to be a substitution derivative of Fritsche's compound. It crystallises in long needles, is soluble in alcohol, insoluble in water, and melts at 195°. It dissolves in alkalis and acids, but without forming salts. The investigation is being continued. L. T. T.

Paratolylglyoxylic, Paratolylhydroxyacetic, and Paratolylacetic Acids. By A. Claus and K. Kroseberg (*Ber.*, **20**, 2048—2052).—Contrary to the statement made by Anschütz and Schönfeld (Abstr., 1886, 786), the authors find that amyl chloroxalate is formed

when amyl oxalate is heated with phosphorus pentachloride, and have in consequence been able to compare Roser's paratoluylcarboxylic acid (Abstr., 1883, 194) with the product obtained by them by the action of aluminium chloride on a mixture of toluene and ethyl chloroxalate. Paratolylglyoxylic acid seems to have no sharp melting point, inasmuch as it begins to soften at 80°, is partially fused at 95°, and is completely melted at 100°. It is not volatile with steam at ordinary pressure, but is completely decomposed by superheated steam. The *potassium*, *sodium* (with $\frac{1}{2}$ mol. of H_2O), *barium*, *calcium* (with 1 mol. of H_2O), *copper*, *lead*, and *silver* salts are described. The *chloride* could not be isolated in the pure state, but the *amide*, $C_9H_7O_2{\cdot}NH_2$, obtained by saturating the benzene solution of the impure chloride with dry ammonia, crystallises in transparent, yellow, prismatic forms, melts at 160°, and is soluble in alcohol. The *ethyl* salt is a yellow oil, boils at 260—270°, and has a fruity odour.

Paratolylhydroxyacetic acid, $C_6H_4Me{\cdot}CH(OH){\cdot}COOH$, is readily obtained by the reduction of paratolylglyoxylic acid with sodium amalgam or zinc-dust. It crystallises in large tables, melts at 145—146°, and is soluble in alcohol, ether, chloroform, and benzene, sparingly soluble in cold water and insoluble in light petroleum. Its salts are not well characterised; the *ethyl* salt crystallises in colourless tufts of needles, melts at 77°, and is soluble in ether.

Paratolylacetic acid, $C_6H_4Me{\cdot}CH_2{\cdot}COOH$, is formed when paratolylglyoxylic acid is treated with warm water, red phosphorus, and iodine. It forms colourless crystals, melts at 74°, and is readily soluble in ordinary organic solvents and in hot water. The *sodium* (with 1 mol. of H_2O), *barium* (with 2 mols. of H_2O), and *calcium* (with 2 mols. of H_2O) salts are readily soluble in water; the *ethyl* salt boils at 240°.

Steinicke, at the suggestion of Claus, has repeated the experiments of Buchka and Irish on the oxidation of paratolyl methyl ketone with potassium ferricyanide (this vol., p. 825), and also finds that an acid not volatile with steam is one of the products, but the yield is small and the acid has not been obtained free from nitrogen, whilst in addition its barium salt differs from that of paratolylglyoxylic acid. Inasmuch as paratolyl methyl ketone, when oxidised with potassium permanganate, does not yield paratolylglyoxylic acid, the law that aromatic ketones containing a side-chain in the ortho-position to the ketonic group are alone oxidised by potassium permanganate to α-ketonecarboxylic acids (*Ber.*, **19**, 234) still holds good.

W. P. W.

Paratolylglyoxylic Acid. By K. Buchka (*Ber.*, **20**, 2213—2214). —A reply to Claus (preceding Abstract) in which the author asserts the accuracy of his results (this vol., p. 825) and the inaccuracy of the work brought forward in opposition.

Behaviour of Ethyl Oxalate towards Resorcinol. By A. Michael (*J. pr. Chem.* [2], **35**, 510—512).—Ethyl oxalate (1 mol.) is added to a solution of resorcinol (1 mol.) and sodium ethoxide (2 mols.) in absolute alcohol; after 4 or 5 days, water is added, and the yellow, crystalline precipitate so formed crystallised from alcohol.

It forms pale-yellow prisms melting at 253—256° with decomposition, insoluble in water, readily soluble in hot alcohol; it is also soluble in alkali. Analyses point to the formula $C_{14}H_{10}O_6$. The *acetyl-derivative*, $C_{14}H_7Ac_3O_6$, crystallises in white prisms melting at 125—127°; it is readily soluble in hot alcohol. The compound has probably the constitution

$$O<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>C(OH)\cdot COOH, \text{ or } C_6H_3(OH)_2\cdot C(OH)<\begin{matrix}C_6H_3(OH)\\CO\text{———}\end{matrix}>.$$

N. H. M.

Tannic Acid in Mountain Ash Berries. By C. Vincent and Delachanal (*Bull. Soc. Chim.*, **47**, 492—493). The juice of the ripe berries of *Sorbus aucuparia* contains a new tannin, *sorbitannic acid*, closely allied in its reactions to morintannic and caffetannic acids. To separate it, the juice is fermented to remove glucose, a small amount of lead acetate is added, the precipitate filtered off and excess of basic lead acetate added, the voluminous yellow precipitate formed is collected, well washed, and decomposed with hydrogen sulphide, and the clear solution evaporated to dryness in a vacuum. The residue is then extracted with absolute alcohol, and the alcoholic extract evaporated, when the tannic acid is obtained as a very thick, syrupy mass. It gives an intense yellow coloration with alkalis, which, however, disappears on the addition of an acid. Ne precipitate is formed with alum. It reduces silver salts and yields an olive-green precipitate with cupric acetate; with iron salts, it gives a very intense dark-green coloration which on the addition of alkalis turns to a reddish-brown; neutral lead acetate forms a yellow precipitate, and the basic acetate yields a citron-yellow precipitate; neither gelatin nor salts of quinine give any precipitate. When heated with dilute sulphuric acid, a reddish-yellow coloration appears, but no precipitate is formed; nitric acid gives rise to a deep yellow coloration. On distillation, a thick brown distillate is obtained containing much pyrocatechol, a voluminous coke being left; fused with potash, pyrocatechuic acid and phloroglucol are formed. A. P.

Action of Arsenious Sulphide on the Acid Chlorides. By B. Rayman (*Bull. Soc. Chim.*, **47**, 896—898).—*Benzoyl thioarsenite*, $As(S\cdot COPh)_3$, is obtained by gently heating benzoic chloride with arsenious sulphide, and extracting the result with alcohol, ether, or carbon bisulphide. It crystallises in large, rose-coloured needles, melts at 178—179°, dissolves in warm ammonia, and is precipitated unaltered on the addition of hydrochloric acid; if, however, the solution is left for some time, it is decomposed, arsenious sulphide being precipitated, and hydrogen sulphide being given off. On heating benzoyl thioarsenite with aniline, a similar reaction takes place, benzanilide being formed. A cold solution of benzoyl thioarsenite in ammonia is precipitated on the addition of solutions of the salts of the heavy metals; mercuric chloride yields a white precipitate of *mercury α-thiobenzoate*, $(PhCO\cdot S)_2Hg$: this crystallises from boiling alcohol in slender colourless needles. Under similar circumstances salts of bismuth yield a white precipitate which becomes brown after

a while; salts of cadmium also yield a white precipitate, which when recrystallised from boiling alcohol is obtained as a yellow compound, containing cadmium, sulphur, and arsenic: the precipitate formed by salts of nickel is brick-red; the silver compound decomposes violently.

Phthalyl chloride acts on arsenious sulphide at elevated temperatures, arsenious chloride being formed and *thiophthalic anhydride*, $C_6H_4<\begin{matrix}CS\\CO\end{matrix}>O$; the latter is a yellow substance, which melts at 114°, distils at 278°, and volatilises with aqueous vapour. When heated with resorcinol, it gives a fluorescent substance, whilst with aniline and toluidine, hydrogen sulphide is evolved, and the compound $C_6H_4<\begin{matrix}(NPh)\\-CO-\end{matrix}>O$ is formed. A. P.

Phthalaldehydic Acid. By S. Racine (*Annalen*, **239**, 78—91).—The preparation and properties of α-bromophthalide and of phthalaldehydic acid have been previously described by the author (Abstr., 1886, 549). The acid crystallises in monoclinic plates and melts at 97°. The *calcium* salt, $Ca(C_8H_5O_3)_2+2H_2O$, forms monoclinic prisms, sparingly soluble in cold water. The *silver* salt, $AgC_8H_5O_3$, is deposited from a hot aqueous solution in slender needles. The *ethyl* salt, $EtC_8H_5O_3$, crystallises in needles. It melts at 66° and, like the free acid, reduces ammoniacal silver solutions, and combines with hydroxylamine. The *methyl* salt, $MeC_8H_5O_3$, melts at 44°. The acetyl derivative melts at 60—63°, and is soluble in alcohol, ether, and chloroform.

Phthalaldehydic acid unites with hydroxylamine, forming *benzaldoximorthocarboxylic* acid, and with phenylhydrazine, forming a colourless crystalline compound, $C_{14}H_{10}N_2O$, melting at 105°. On reduction with tin and hydrochloric acid, phenylphthalimidine, $C_{14}H_{11}NO$, is obtained.

Hydrobenzamidtricarboxylic acid, $N_2(CH\cdot C_6H_4\cdot COOH)_3$, precipitated when gaseous ammonia is passed into an alcoholic solution of phthalaldehydic acid. It melts at 187°. A condensation product, *orthobenzylidenecarboxylic acid*, is formed on mixing alcoholic solutions of aniline and phthalaldehydic acid. The acid is insoluble in water but sparingly soluble in alcohol. It melts at 174°, and unites directly with two atoms of bromine, forming a crystalline compound.

Diphthalide ether, $<\begin{matrix}C_6H_4\\CO\cdot O\end{matrix}>CH\cdot O\cdot CH<\begin{matrix}C_6H_4\\O\cdot CO\end{matrix}>$, formed as a bye-product in the preparation of phthalaldehydic acid, is a colourless crystalline compound melting at 221°. It does not exhibit aldehydic reactions. *Amidophthalide*, $C_6H_4<\begin{matrix}CH(NH_2)\\-CO\cdot O-\end{matrix}>$, is precipitated when gaseous ammonia is passed into a solution of bromophthalide in benzene or ether. Amidophthalide melts at 167° and dissolves in alcohol, ether, benzene, chloroform, and in hot water and alkalis. It is re-precipitated from the alkaline solutions by acids. W. C. W.

Benzyl and Benzoyl Compounds. By C. A. Bischoff and H. Siebert (*Annalen*, **239**, 92—110).—Conrad (Abstr., 1879, 707)

prepared ethyl benzylmalonate by the action of benzyl chloride on ethyl sodiomalonate, but he overlooked the formation of small quantities of ethyl dibenzylmalonate. *Benzylmalondiamide*,

$$C_7H_7CH(CONH_2)_2,$$

is obtained by heating alcoholic ammonia and ethyl benzylmalonate at 160°. The mother-liquor contains the monamide of ethyl benzylmalonate, $NH_2{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOEt$. The former compound melts at 225°, and the latter at 98°.

Ethyl dibenzylmalonate, $C(C_7H_7)_2(COOEt)_2$, is a thick oil. On treatment with alcoholic ammonia, it yields a mixture of benzylmalondiamide and the monamide of ethyl benzylmalonate and other products. On hydrolysis with alcoholic potash, 40 grams of ethyl dibenzylmalonate yielded 20·5 grams of dibenzylmalonic acid and 5 grams of dibenzylacetic acid. *Dibenzylmalonic acid* melts at 162°, with evolution of carbonic anhydride. It is soluble in ether, alcohol, acetone, benzene, and is sparingly soluble in cold water and hot light petroleum. The acid crystallises from alcohol in thick prisms, from ether in plates, and from hot water in slender needles. The ammonium salt produces crystalline precipitates in solutions of lead acetate, calcium chloride, and barium chloride, and amorphous precipitates with mercuric chloride, zinc sulphate, and silver nitrate. Dibenzylacetic acid has been already described by Ehrlich (*Ber.*, **6**, 1085; *Annalen*, **187**, 21).

The chief product of the action of orthonitrobenzoic chloride on ethyl sodium benzylmalonate is ethyl orthonitrobenzoylbenzylmalonate, ethyl dibenzylmalonate, and ethyl benzylacetate. Ethylic orthonitrobenzoylbenzylmalonate, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C(C_7H_7)(COOEt)_2$, is also formed by the action of benzyl chloride on the yellow sodium compound of ethyl mononitrobenzoylmalonate. It melts at 94°, and decomposes at a higher temperature with evolution of carbonic anhydride. It is freely soluble in ether, benzene, acetone, glacial acetic acid, and in hot alcohol. The production of this compound by these two reactions shows that in the yellow sodium compound of ethyl mononitrobenzoylmalonate described by Bischoff and Rach (Abstr., 1885, 264) the sodium is directly attached to a carbon-atom, thus: $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CNa(COOEt)_2$.

Ethyl orthonitrobenzoylbenzylmalonate yields on saponification with potassium hydroxide, benzylmalonic and orthonitrobenzoic acids, and on treatment with alcoholic ammonia it is converted into orthonitrobenzamide. W. C. W.

Combination of Lactones with Ethereal Salts. By W. Wislicenus (*Ber.*, **20**, 2061—2062).—Sodium is without action on a mixture of equimolecular proportions of phthalide and ethyl oxalate in ethereal solution, if these compounds are free from alcohol, but yields an intensely yellow-coloured precipitate when alcohol is present. This compound is best obtained by adding an ethereal solution of phthalide (1 mol.) to an ethereal solution of sodium ethoxide free from alcohol (1 mol.) and ethyl oxalate (1 mol). The mixture is then allowed to remain for some hours. The yellow product is a sodium

compound, and on treatment with an acid yields a compound of the formula $C_{12}H_{10}O_5$. This crystallises from ether in small, slender needles and from alcohol in glistening scales, melts at 121—122°, and is insoluble in water. Its solution in alkalis very readily reduces Fehling's solution at the ordinary temperature, whilst the alcoholic solution is coloured a dark violet-red by ferric chloride.

The foregoing reaction is probably of general application, inasmuch as phthalide and ethyl benzoate yield a yellow compound which reduces Fehling's solution, and valerolactone and ethyl oxalate form a colourless sodium compound under similar conditions. W. P. W.

Nitro-ψ-cumidinesulphonic Acid. By F. Mayer (*Ber.*, **20**, 2066—2068).—Further investigation has shown that the acid obtained when trinitro-ψ-cumene is reduced with hydrogen sulphide can be diazotised without displacement of the sulphonic group; the author, therefore, considers it to be a nitro-ψ-cumidinesulphonic acid (compare this vol., p. 659).

Diazonitro-ψ-cumenesulphonic acid, $NO_2{\cdot}C_6Me_3{<}^{N:N}_{-SO_3}{>}$, obtained as a colourless precipitate on diazotising sodium nitro-ψ-cumidinesulphonate, is a comparatively stable compound which does not evolve nitrogen when boiled with alcohol under 250 mm. pressure, and decomposes extremely slowly when boiled with water. On treatment with β-naphthol dissolved in dilute aqueous potash, it yields *β-naphtholazonitro-ψ-cumenesulphonic acid*, $C_{19}H_{17}N_3SO_6 + 2H_2O$, which crystallises in orange scales showing a metallic lustre, and sparingly soluble in water. The alkaline salts are dark-red in colour, and moderately soluble. The *calcium* salt crystallises in red scales showing a metallic lustre. W. P. W.

Aromatic Thiosulphonates containing Bivalent Alkyl-radicles. By R. Otto and A. Rössing (*Ber.*, **20**, 2079—2088).—*Ethylene thiobenzenesulphonate*, $C_2H_4 : S_2(SO_2Ph)_2$, is obtained when an alcoholic solution of potassium thiobenzenesulphonate (2 mols.) is heated with ethylene dibromide (1 mol.) at 100° for some hours in a reflux apparatus, until all odour of the dibromide has disappeared. It crystallises in small, slender, transparent, silky needles, is destitute of odour and taste, melts at 84—85°, and is readily soluble in benzene and hot alcohol, insoluble in water. On treatment in alcoholic solution with potassium hydroxide at 100°, until permanent alkalinity is produced, ethylene thiobenzenesulphonate yields a mixture of potassium benzenesulphinate, potassium ethylenedisulphinate, and diethylene tetrasulphide; and inasmuch as the addition of ethylene mercaptan to a warm alcoholic solution of ethylene thiobenzenesulphonate brings about the production of benzenesulphinic acid and diethylene tetrasulphide, the authors regard this reaction as taking place in two stages:—I. $C_2H_4 : S_2(SO_2Ph)_2 + 4H_2O = 4PhSO_2H + C_2H_4(SO_2H)_2 + C_2H_4(SH)_2$; II. $C_2H_4 : S_2(SO_2Ph)_2 + C_2H_4(SH)_2 = 2Ph{\cdot}SO_2H + (C_2H_4S_2)_2$. The salt is also readily saponified by barium hydroxide, or when heated with aqueous ammonia at 110° in sealed tubes. If the hydrolysis is effected by means of potas-

sium sulphide, potassium thiobenzenesulphonate and potassium mercaptide are obtained, and the reaction corresponds with that occurring when monovalent alkyl salts are similarly treated (this vol., p. 226). When reduced with zinc and hydrochloric acid, ethylene thiobenzenesulphonate yields diethylene tetrasulphide and thiophenol, the latter doubtless resulting from the reduction of benzenesulphinic acid; if it is heated in alcoholic solution with zinc-dust at 110° for two hours, it is converted into zinc benzenesulphinate and zinc mercaptide.

Ethylene thioparatoluenesulphonate is obtained in like manner by heating equivalent quantities of ethylene bromide and potassium thioparatoluenesulphonate in alcoholic solution. It crystallises in colourless, transparent needles having pyramidal terminations, and showing a vitreous lustre, melts at 76—77°, has neither odour nor taste, and is readily soluble in benzene and hot alcohol, soluble in ether, insoluble in water. When saponified with potassium hydroxide, it yields diethylene tetrasulphide and potassium paratoluenesulphinate.

The following details are given in various footnotes:—Potassium thiobenzenesulphonate, with 2 mols. H_2O; the sodium salt, with $1\frac{1}{2}$ mols. H_2O; potassium benzenesulphinate, with 2 mols. H_2O; and the sodium salt, with 2 mols. H_2O, are described; and the optical properties of the crystals of the first and last salts are given. Ethylene mercaptan, when treated with ammonia and exposed to the air for some time, is converted into a compound melting between 86° and 90°.

Mixed alkyl tetrasulphides can be obtained from sulphinic acids and mercaptans containing bivalent radicles: thus, to judge from its decomposition products, ethylene diphenyltetrasulphide,

$$Ph{\cdot}S_2{\cdot}C_2H_4{\cdot}S_2{\cdot}Ph,$$

appears to be formed by the action of ethylene mercaptan (1 mol.) on benzenesulphinic acid (2 mols.) in alcoholic solution (compare this vol., p. 242).

Pure diethylene tetrasulphide melts at 148—151° without carbonisation (compare this vol., p. 463). W. P. W.

Reduction of Aromatic Thiosulphonates containing Univalent and Bivalent Alkyl-radicles with Hydrogen Sulphide. By R. Otto and A. Rössing (*Ber.*, **20**, 2090—2092).—When phenyl thiobenzenesulphonate in dilute alcoholic solution is reduced with hydrogen sulphide, thiophenol and sodium benzenesulphonate are obtained, together with a viscous oil of unpleasant odour; this is a phenyl polysulphide, probably the tetrasulphide (compare preceding Abstract), inasmuch as it is reduced to phenyl bisulphide on treatment with colourless ammonium sulphide. Tolyl parathiotoluenesulphonate when similarly treated yields paratolyl bisulphide, tolyl tetrasulphide, and paratoluenesulphinic acid; thiocresol is probably formed in the reaction, but is not found among the products, owing to the readiness with which it reacts with toluenesulphinic acid to form tolyl bisulphide. Ethyl thiobenzenesulphonate under these conditions is converted into ethyl mercaptan, benzenesulphinic acid, and a phenyl polysulphide, which is reduced to phenyl bisulphide on

treatment with colourless ammonium sulphide. Ethylene thiobenzenesulphonate when suddenly reduced yields ethylene mercaptan, phenyl tetrasulphide, and a substance insoluble in hot alcohol, which most probably consists of the products obtained by the action of ethylene mercaptan on benzenesulphinic acid (see p. 954).

W. P. W.

Halogen-derivatives of Phenylene Dichloracetylene Ketone. By T. Zincke and C. Frölich (*Ber.*, **20**, 2053—2057).—*Phenylene tetrachlorethylene ketone* (tetrachlorhydrindonaphthene ketone),

$$C_6H_4<\begin{matrix}CO-\\CCl_2\end{matrix}>CCl_2,$$

is formed when an acetic acid solution of phenylene dichloracetylene ketone is treated with chlorine until the yellow colour is no longer visible; the solution after remaining some time in a closed vessel is then allowed to evaporate at the ordinary temperature. It crystallises in large, colourless, transparent, monoclinic forms, or in thick, white, striated needles, melts at 107—108°, but sublimes at a lower temperature with an odour resembling that of hexachlorethane, and is soluble in alcohol and acetic acid. Sulphurous acid and potassium iodide are without action on the tetrachloro-ketone, but stannous chloride converts it into the dichloro-derivative, whilst hydroxylamine hydrochloride does not combine with it until the two compounds are heated at 120—160°, when the oxime of the dichloro-ketone is obtained.

Orthotrichlorovinylbenzoic acid, $CCl_2:CCl\cdot C_6H_4\cdot COOH$, is obtained if the tetrachloro-ketone is carefully heated with aqueous soda and a small quantity of alcohol, or if the warm alcoholic solution is added to cold aqueous soda. It crystallises in colourless needles or broad scales, melts at 163°, sublimes at higher temperatures without decomposition, and is soluble in alcohol and acetic acid. The *methyl* salt forms large, colourless, monoclinic (?) tables or prisms, and melts at 68°. Neither chlorine nor bromine additive compounds of the acid have been obtained, but 1 : 2 ethylbenzoic acid, melting at 68°, is formed on treating it with sodium amalgam in the presence of water.

Phenylene dibromodichlorethylene ketone, $C_6H_4<\begin{matrix}CO-\\CClBr\end{matrix}>CClBr$, is prepared from the dichloro-ketone in a similar manner to the tetrachloro-ketone, bromine being used instead of chlorine, and is crystallised from acetic acid, inasmuch as partial decomposition into bromine and dichloro-ketone occurs if alcohol and ether are employed as solvents. It resembles the tetrachloro-ketone in crystalline form, melts at 125—128° when rapidly heated, but when cooled and reheated, or when heated slowly, the melting point is 113—114°. Sulphurous acid and stannous chloride convert it into the dichloro-ketone, hydroxylamine hydrochloride and aniline in alcoholic solution convert it on boiling into the oxime and anilide of the dichloro-ketone respectively, whilst iodine is liberated from alcoholic potassium iodide by its action.

Orthodichlorobromovinylbenzoic acid, $CClBr:CCl\cdot C_6H_4\cdot COOH$, prepared similarly to the trichloro-compound, forms colourless needles,

melts at 173—174°, and is readily soluble in alcohol. The *methyl* salt crystallises like the trichloro-salt, and melts at 82°. Neither chlorine nor bromine additive compounds of the acid have been obtained, but sodium amalgam readily reduces it to 1 : 2 ethylbenzoic acid. W. P. W.

Indoles. By A. Pfülf (*Annalen*, **239**, 220—223).—Fischer and Hess (Abstr., 1884, 1181) have pointed out that phenylindolecarboxylic acid decomposes at 200° into phenylindole and carbonic anhydride. The indole is a pale-yellow oil boiling at 326—327°, soluble in alcohol, ether, and benzene. It does not form a compound with picric acid.

Sodium hypochlorite precipitates from a cold neutral solution of phenylindolecarboxylic acid, [Ph : COOH = 1′ : 2′], a red, resinous mass which after a time becomes crystalline.

Phenylpseudoisatin, $C_6H_4<^{CO\cdot CO}_{-NPh-}>$, is extracted from the alcoholic solution of this crude product by boiling it with alcoholic soda, removing the alcohol by evaporation, dissolving the residue in water, and precipitating the isatin by hydrochloric acid. Phenylpseudoisatin is deposited from ethereal solutions in red plates. It melts at 134°, and dissolves freely in alcohol, ether, and benzene.

Acetophenonephenylhydrazine melts at 97—98°, and is converted into diphenylindole [1′ : 2′] by the action of zinc chloride. This indole boils above 360°, and has not yet been obtained in the crystalline state. It is soluble in alcohol, ether, and benzene, and does not combine with picric acid. W. C. W.

Indoles from Tolylhydrazines. By J. Raschen (*Annalen*, **239**, 223—229).—*Paratolylhydrazinepyruvic acid* separates as a yellow, crystalline precipitate on adding an aqueous solution of paratolylhydrazine hydrochloride to pyruvic acid. The acid melts with decomposition at 158—160°. It is soluble in alcohol, chloroform, and acetic acid. The *ethylic* salt crystallises in needles of a pale-yellow colour. It is converted into the ethylic salt of methylindolecarboxylic acid by the action of zinc chloride at 220°. 3 : 2′ *Methylindolecarboxylic acid* melts at 227—228° with evolution of carbonic anhydride and formation of methylindole [Me = 3] and other products. The acid is freely soluble in alcohol, ether, chloroform, and acetic acid. The *ethylic* salt forms colourless needles or plates melting at 158—160°. 3-*Methylindole* is soluble in alcohol, ether, benzene, light petroleum, and in hot water. It melts at 58·5°, and closely resembles indole in its reactions with pine-wood, and with nitrous and picric acids. The *picrate*, $C_9H_9N,C_6H_2(NO_2)_3\cdot OH$, is deposited from a hot aqueous solution as it cools in red needles melting at 151°.

Paratolylhydrazine-acetone melts at 50—52°. On exposure to the air, it deliquesces and forms a resinous mass.

3 : 2′-*Dimethylindole* melts at 114—115°, and boils without decomposition. It is freely soluble in warm alcohol, benzene, ether, and glacial acetic acid. The *picrate*, $C_{10}H_{11}N\cdot C_6H_2(NO_2)_3OH$, is deposited from benzene in dark-red needles. This salt melts at 155°.

Orthotolylhydrazinepyruvic acid melts at 158—159° with decomposition. The *ethyl* salts melts at 61—62°, and is deposited from hot alcoholic solutions in slender needles of a pale-yellow colour. 1 : 2′ Methylindolecarboxylic acid melts at 170—171° with decomposition, yielding a very small quantity of methylindole. The acid is soluble in alcohol, ether, acetic acid, and in hot water.

W. C. W.

Methylindoles. By M. Wenzing (*Annalen*, **239**, 239—247).—The preparation of skatole from propylidenephenylhydrazine has been previously described by E. Fischer (Abstr., 1886, 806). The *hydrochloride*, $(C_9H_9N)_2,HCl$, is precipitated from its alcoholic solution by ether in white, needle-shaped crystals. It melts at 167—168°. The picrate contains picric acid and skatole in molecular proportion. *Benzylidenediskatole* is formed by the action of zinc chloride on benzaldehyde and skatole. It melts at 140—142°, and dissolves in hot alcohol, chloroform, ether, and acetic acid. It does not yield benzaldehyde when boiled with hydrochloric or sulphuric acids. *Hydroskatole* formed by reducing an alcoholic solution of skatole with zinc-dust and hydrochloric acid, is a colourless oil resembling quinoline and piperidine in odour. It boils at 231—232° under 744 mm. pressure (thermometer immersed in vapour). It dissolves freely in alcohol, ether, and light petroleum, and the alcoholic solution stains pine-wood of an orange colour. The *hydrochloride* is soluble in water and alcohol, but insoluble in ether. The *oxalate* melts at 126° with decomposition, and is insoluble in ether. The *picrate* is deposited from benzene in yellow granular crystals melting at 149—150°. The *platinochloride*, $(C_9H_{11}N)_2,H_2PtCl_6$, forms yellow needles and is sparingly soluble in water. It is decomposed by hot water. Hydroskatole yields a nitroso-derivative. It is an oily liquid, and yields a hydrazine on reduction which forms a crystalline sulphate.

Hydromethylketole and the nitrosamine have been described by Jackson (Abstr., 1881, 734). Hydromethylketole boils at 227—228° under 742 mm. pressure. The oxalate and picrate are crystalline, and melt at 130° and 150° respectively. The *hydrazine* forms colourless prisms soluble in alcohol, ether, and light petroleum. It melts at 40—41°, and yields a crystalline sulphate and hydrochloride soluble in alcohol. Hydromethylketole forms a crystalline compound, $C_{16}H_{16}N_2S$, with phenyl thiocyanate. It is soluble in ether, and melts at 100—101°.

Hydromethylindole [Me = 1′] boils at 216° under 728 mm. pressure, and is volatile in a current of steam. It is soluble in alcohol and ether. Most of its salts are soluble in alcohol and water. The *platinochloride*, $(C_9H_{11}N)_2,H_2PtCl_6$, is decomposed by boiling in water. The *oxalate* melts at 103—105°, and the *picrate* at 155°.

W. C. W.

Condensation of Isobutaldehyde and Methylal with Aniline. By W. v. Miller and F. Kinkelin (*Ber.*, **20**, 1934—1942).—The author investigated this reaction in the hope of obtaining an indole according to the reactions: $CHMe_2{\cdot}COH + CH_2O = CHMe_2{\cdot}CH(OH){\cdot}COH$ and $CHMe_2{\cdot}CH(OH){\cdot}COH + C_6H_5{\cdot}NH_2 =$

$CH\langle \begin{matrix} CPr^{\beta}\cdot C\cdot CH:CH \\ \| \\ -NH\cdot C\cdot CH:CH \end{matrix} \rangle + 2H_2O$. The product of the reaction had no odour of indole, but yielded a base which, when heated with zinc chloride, gave small quantities of an indole, probably of the above formula. Besides this indole, the author obtained from the zinc chloride melt two isomeric bases, $C_{11}H_{11}N$, and a base, $C_{13}H_{15}N$. The bases, $C_{11}H_{11}N$, the author believes to be dimethylquinolines. The one is solid, melts at 63—65°, and boils at 274—275°; the other is liquid, and boils about 265—275°. The base, $C_{13}H_{15}N$, boils about 300°. All are being investigated. L. T. T.

Diphenylenedihydrazine. By R. Arheidt (*Annalen*, **239**, 206—215).—*Diphenylenedihydrazine*, $C_{12}H_8(N_2H_3)_2$, is prepared by reducing the diazo-compound of diamidodiphenyl with sodium sulphite or stannous chloride. The salts of the base are crystalline; the nitrate is freely soluble in hot water; the sulphate and hydrochloride are sparingly soluble. The base is precipitated from solutions of its salts by alkalis and also by sodium acetate. It melts with decomposition at 165—167°, and dissolves sparingly in alcohol, ether, and chloroform. The addition of the theoretical quantity of an aqueous solution of potassium cyanate converts diphenylenedihydrazine hydrochloride into *diphenylenedisemicarbazide*, $C_{12}H_8(NH\cdot NH\cdot CONH_2)_2$. This compound is soluble in glacial acetic acid. It melts with decomposition between 306° and 308°. The sulphate and hydrochloride are crystalline. *Diphenylenedinitrosohydrazine*, $C_{12}H_8(N_2H_2\cdot NO)_2$, melts with decomposition at 112—113°. It is soluble in acetone, chloroform, and acetic acid, but the solutions are unstable. *Diphenylenedihydrazine-pyruvic acid*, $C_{12}H_8(N_2H:CMe\cdot COOH)_2$, is freely soluble in acetone and in alkalis. It melts at 197—198° with decomposition. *Diphenylenediacetonehydrazine*, $C_{12}H_8(N_2H:CMe_2)_2$, is very unstable. It is freely soluble in alcohol, chloroform, and acetic acid, and melts with decomposition at 197—199°. It is converted into *diphenyldimethylindole*, $C_6H_5\cdot C_6H_3\langle \begin{matrix} CH \\ NH \end{matrix} \rangle CMe$, and diphenyl by the action of zinc chloride at 215°. Diphendimethylindole melts at 270°, and boils without decomposition. It is freely soluble in alcohol and acetic acid and exhibits the characteristic indole reaction. W. C. W.

Orthodibenzyldicarboxylic Acid. By N. Dobreff (*Annalen*, **239**, 65—71).—In addition to the salts of orthodibenzyldicarboxylic acid, which have been previously described by Graebe, the author has prepared the following salts:—The ammonium salt, $C_{16}H_{12}O_4(NH_4)_2$, is very soluble in water; the calcium and barium salts are also very soluble, and crystallise with difficulty. The ammonium salt precipitates basic salts from solutions of lead, copper, and zinc acetates. The *methyl* salt, $C_{16}H_{12}O_4Me_2$, melts at 100—101° and is freely soluble in methyl alcohol, alcohol, chloroform, and carbon bisulphide. The *ethyl* salt, $C_{16}H_{12}O_4Et_2$, crystallises in needles or prisms and melts at 69—71°. It is best recrystallised from hot amyl alcohol. On saturating the alcoholic solution with ammonia gas, crystals of ethyl dibenzyldicarb-

oxylaminate, $COOEt{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CONH_2$, are slowly deposited. The compound melts between 65° and 68°.

Dibenzyldicarboxylic acid yields diphthalylic acid when oxidised with potassium permanganate, and stilbene when distilled with soda-lime. Fuming nitric acid converts diphenyldicarboxylic acid into a dinitro-product which is soluble in hot water and in hot alcohol. The calcium and barium salts are amorphous, and explode when heated. The ethyl salt, $C_{16}H_{11}(NO_2)_2O_4Et$, melts at 60°.

On oxidation with potassium permanganate, dinitrobenzyldicarboxylic acid yields β-nitrophthalic acid. W. C. W.

So-called Carbonylcarbazole (Carbazole-blue). By E. Bamberger and R. Müller (*Ber.*, **20**, 1903—1907).—Suida first described this compound (Abstr., 1880, 245) as an anhydride of orthamidophenylbenzoic acid, giving it the formula $<\begin{matrix}C_6H_4{\cdot}NH\\C_6H_4{\cdot}CO\end{matrix}>$. The authors have re-examined it, and find it to belong to the class of triphenylmethane colouring matters, and to have the constitution

$$OH{\cdot}C\left(C_6H_3<\begin{matrix}NH\\C_6H_4\end{matrix}>\right)_3.$$

The authors consider the blue colour of the free base to be only superficial and due to impurities, and on the addition of strong hydrochloric acid it is very much intensified owing to the formation of the true dehydrated colouring matter. When treated with acetic acid and zinc, the *leuco-base* is obtained, which crystallises in microscopic needles, dissolves in ether to a bluish-violet fluorescent liquid, and is reconverted into the colour-base by oxidation. When heated alone or with zinc-dust, the colouring matter yields carbazole. A very similar substance was also prepared by fusing carbon hexachloride with carbazole. The authors therefore propose the name *carbazole-blue* for this substance. L. T. T.

The Hydrocarbon $C_{16}H_{12}$ from Styrolene Alcohol. By T. Zincke (*Annalen*, **240**, 137—147).—In the light of the formation of naphthalene-derivatives by condensation lately observed, and especially of the formation of α-naphthol from phenylisocrotonic acid (Fittig and Erdmann, Abstr., 1885, 545), the author believes the hydrocarbon obtained from styrolene alcohol (phenylglycol) to be β-phenylnaphthalene [Ph = 2], and not to have the formula $<\begin{matrix}CPh:CH\\CH:CPh\end{matrix}>$ previously (Abstr., 1885, 269) ascribed to it. The derivatives will thus be *β-phenylnaphthaquinone*, *β-phenylamidonaphthaquinone*, &c., the constitution of the last-named, for instance, being [O : Ph : NH_2 : O = 1 : 2 : 3 : 4]. This constitution will more fully explain the reactions of this hydrocarbon than the one previously given. The one piece of evidence that seems to be antagonistic to the naphthalene formula—that is, the formation of 0·9 gram of benzoic acid from 1 gram of the hydrocarbon—is probably due to an error in weighing, 2 grams having most likely been really taken. A repetition of the experiment yielded the lower percentage of benzoic acid. The formation (*loc. cit.*) of

phthalic acid and the acid $C_9H_6O_5$ (probably $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$) points to the correctness of the naphthalene formula.

All attempts to synthesise β-phenylnaphthalene by other methods for comparison with the above hydrocarbon gave negative results. Graebe has described (*Ber.*, **7**, 792) a phenylnaphthalene which is probably the α-naphthalene. Watson Smith has described a β-phenylnaphthalene obtained by the action of bromobenzene on naphthalene (Abstr., 1880. 125, 261; see also Smith and Takamatsu, Trans., 1881, 546). The author questions the correctness of Smith's view and believes the compound rather to be the (perhaps impure) α-derivative.

L. T. T.

Action of Chlorine on Phenols. By T. Zincke (*Ber.*, **20**, 2058—2061).—In certain cases, chlorinated ketones are formed when phenols dissolved in acetic acid are treated with chlorine. Definite results have been obtained with the two naphthols, but so far the attempts made to isolate the products of the action of chlorine on hydroxyquinoline, thymoquinone, catechol, and resorcinol have not met with success.

When α-naphthol is treated with chlorine in acetic acid solution, a compound is obtained, which appears to be a chloride of dichloro-β-naphthaquinone, $C_6H_4<\begin{matrix}CO{\cdot}CCl_2\\CCl{\cdot}CCl\end{matrix}>$. It crystallises in large, colourless, rectangular tables, melts at 156—157°, is not decomposed on heating, and is sparingly soluble in ether and light petroleum, readily soluble in benzene and hot alcohol. Although insoluble in dilute alkali it dissolves slowly in concentrated alkali on addition of alcohol, and is converted into phenylenedichloracetyleneglycollic acid (this vol., pp. 54, 728). When the ketone chloride is dissolved in hot alcohol and treated with dilute aqueous soda until the reaction is feebly alkaline, a compound is formed which, on the addition of an acid, separates in slender, orange needles melting at 146°. This is probably a hydroxy-derivative obtained by the substitution of hydroxyl for chlorine in the ketone chloride; it dissolves without decomposition in cold dilute alkali with a yellow colour, but on heating the solution it becomes dark red, and yields chlorhydroxy-α-naphthaquinone (m. p. = 215°) when treated with an acid. Dichloro-β-naphthaquinone and its chloride, therefore, exhibit a similar series of reactions, inasmuch as it is converted into chlorhydroxy-α-naphthaquinone by prolonged treatment with sodium carbonate, or by heating with concentrated hydrochloric acid.

The ketone chloride obtained from β-naphthol under similar conditions crystallises from the acetic acid solution in broad lustrous laminæ, melts at 85°, and is readily soluble in alcohol and acetic acid, but quickly resinifies in these solutions. From benzene and light petroleum, however, it crystallises in small, glistening scales, which melt at 100° to a turbid liquid which becomes clear at 140°. Dilute alkali converts the ketone chloride into black resinous products, but on treating its solution in aqueous alcohol with sodium carbonate, it yields a compound which crystallises in thick, glistening, red needles, melts at 174°, and is soluble in benzene and acetic acid. The investigation will be continued.

W. P. W.

Action of Chlorine on Aceto-β-Naphthylamine. By P. T. Cleve (*Ber.*, **20**, 1989—1992).—*Acetochloro-β-naphthylamine*, $C_{10}H_6Cl\cdot NHAc$, is prepared by passing chlorine (1 mol.) into a solution of aceto-β-naphthylamine in dilute acetic acid, and precipitating with water. It crystallises from alcohol in very slender colourless needles, which melt at 147°; it is sparingly soluble in boiling water, readily in alcohol.

Chloro-β-naphthylamine, $C_{10}H_6Cl_2\cdot NH_2$, is obtained by treating an alcoholic solution of the above acetyl-derivative with hydrochloric acid. It crystallises from dilute alcohol in slender colourless needles, melting at 59°. The *hydrochloride* crystallises (with 1 mol. H_2O) in lustrous colourless needles, rather soluble in boiling water containing hydrochloric acid. When the base is treated with nitrogen trioxide in presence of sulphuric acid, α-chloronaphthalene is formed; when boiled with nitric acid, it is oxidised to phthalic acid.

Dichloronaphthalene, $C_{10}H_6Cl_2$, is formed when 10 grams of chloro-β-naphthylamine hydrochloride dissolved in boiling hydrochloric acid is treated with 5 grams of cuprous chloride, and 4 grams of potassium nitrate dissolved in 20 c.c. of water added by drops. The product is steam distilled, and the yellow oil so obtained, which solidifies in a few days, crystallised from alcohol; it separates in tabular monoclinic crystals; $a : b : c = 1{\cdot}5196 : 1 : ?$; $\beta = 76° 46'$; it melts at 34—35°; Widman's α-dichloronaphthalene melts at 38°, and crystallises in pointed needles.

When monochloronaphthylamine is heated with soda-lime, α-β-naphthazine (Witt, *Ber.*, **19**, 2791) is formed. The dichloronaphthalene described above is therefore an α-β-derivative. N. H. M.

Orthoamidated Aromatic Mercaptans. By P. Jacobson (*Ber.*, **20**, 1895—1903).—The author has previously shown (Abstr., 1886, 700 and 876) that the anhydro-compounds of orthamidophenyl mercaptan are easily formed by the oxidation of thioanilides. He has now extended this reaction to the naphthalene series.

α-Thioacetonaphthalide described by Bernthsen and Trompetter (Abstr., 1879, 146) is best obtained by acting on acetonaphthalide with phosphoric sulphide; it melts at 110—111° (Bernthsen and Trompetter give 95—96°). When oxidised with potassium ferricyanide, this yields ethenylamidonaphthyl mercaptan, $C_{10}H_6{<}\overset{N}{\underset{S}{}}{>}CMe$, probably identical with that recently obtained by Hofmann (this vol., p. 839). The *hydrochloride* crystallises in needles. Benzenylamidonaphthyl mercaptan, also described by Hofmann (*loc. cit.*,) was similarly obtained from α-thiobenzonaphthalide. The *picrate* yields characteristic orange needles, melting at 130—131°. Attempts to prepare amidonaphthyl mercaptan by heating the benzyl base with alcoholic potash were unsuccessful, but a slightly basic oxidation derivative crystallising in yellow scales and melting at 131—132° was obtained. The author is unable at present to decide whether this is a diamidodinaphthyl bisulphide, $S_2(C_{10}H_6\cdot NH_2)_2$, or a thionaphthoquinonimide, $C_{10}H_6{<}\overset{NH}{\underset{S}{}}{>}$, the percentage composition of which are very similar. When treated

with acetic anhydride, this substance yields *diacetylamidonaphthyl mercaptan*, $NHAc{\cdot}C_{10}H_6{\cdot}SAc$, crystallising in long needles, and melting at 173·5—175°. When heated with hydrochloric acid at 200—220°, this acetyl-derivative is decomposed, ethenylamidonaphthyl mercaptan being formed.

Orthamidophenyl mercaptan bisulphide, when heated with acetic anhydride, yields *diacetylamidophenyl mercaptan*, $NHAc{\cdot}C_6H_4{\cdot}SAc$, crystallising in prisms melting at 135°. Phenyl bisulphide and benzyl bisulphide are, however, not attacked by acetic chloride, so that this is not a general reaction for bisulphides, and does not decide which of the two formulæ proposed for the new compound is the correct one.

L. T. T.

Action of Aldehydes on Amidosulphonic Acids. By E. Cahn and M. Lange (*Ber.*, **20**, 2001—2002).—When sodium naphthionate (1 mol.) dissolved in a little water is treated with benzaldehyde (1 mol.) and shaken, the *condensation product* $SO_3Na{\cdot}C_{10}H_6{\cdot}N:CHPh$ separates in straw-coloured plates. This is decomposed into its original constituents by prolonged boiling with water. The corresponding condensation product from α-naphthylaminesulphonic acid and benzaldehyde is prepared by adding the aldehyde to an alcoholic solution of the sodium salt of the sulphonic acid, and crystallises in concentrically grouped needles. The analogous compound from ββ-naphthylaminesulphonic acid and benzaldehyde crystallises in well-formed, long, pale-yellow prisms.

Benzidinesulphonic acid and the sulphonic acid of amido-azo-compounds yield analogous compounds.

N. H. M.

β-Naphthylaminesulphonic Acids. By S. Forsling (*Ber.*, **20**, 2099—2106).—Further examination has shown that the β-naphthylaminesulphonic acid obtained by heating β-naphthylamine with sulphuric acid at 140° (Abstr., 1886, 890), is not pure, but contains three isomerides, of which one is identical with Brönner's acid (this vol., p. 375), and a second, produced in small quantity only, is perhaps identical with the δ-acid (*loc. cit.*, p. 732), whilst the remaining two, designated as 1 and 2, are respectively identical with the acids termed α and γ in a patent specification of Dahl's. A separation of the acids was effected by fractional crystallisation of the calcium salts.

β-Naphthylaminesulphonic acid, 1, dissolves in about 1700 parts of cold water, and is almost insoluble in alcohol. Its salts generally are readily soluble in water, yielding solutions fluorescing blue, and, with the exception of the silver and copper salts, can be heated at 180° without decomposition. The *potassium* salt with $\frac{1}{2}$ mol. H_2O, forms six-sided tables; the *sodium* salt is anhydrous, and crystallises in thin four-sided scales; the *barium* salt, with 4 mols. H_2O, forms long prisms, and dissolves in about 23 parts of cold water; the *calcium* salt, with 6 mols. H_2O, forms large, thick tables, which become coloured red on crystallisation from an aqueous solution, and dissolve in about 11 parts of cold water; the *magnesium* salt, with $3\frac{1}{2}$ mols. H_2O, forms small crystalline aggregates; the *zinc* salt, with 6 mols. H_2O, crystallises in prisms; and the *lead* salt crystallises in small needles, and is anhydrous. The corresponding diazonaphtha-

lenesulphonic acid, $C_{10}H_6N_2SO_3$, a greenish-yellow, indistinctly crystalline powder, yields, when boiled with water, Bayer's β-naphtholsulphonic acid, from which θ-dichloronaphthalene (m. p. 61·5°) is obtained on treating its potassium salt with phosphorus pentachloride.

β-Naphthylaminesulphonic acid, 2, dissolves in about 1300 parts of cold water, and is almost insoluble in alcohol. Its salts dissolve readily in water, yielding solutions fluorescing blue, and show great similarity in properties to the corresponding salts of the No. 1 acid. The *potassium* salt, with 1 mol. H_2O, crystallises in small rhombohedra; the *sodium* salt, with 5 mols. H_2O, crystallises in large tables; the *barium* salt, with $2\frac{1}{2}$ mols. H_2O, forms small aggregates; the *calcium* salt, with 11 mols. H_2O, crystallises in long, yellowish needles, and dissolves in about 11 parts of cold water: the amount of water of crystallisation in this salt varies with the temperature at which crystallisation takes place, and at about 10° crystals are obtained which at once effloresce when separated from the mother-liquor; the *magnesium* salt, with 8 mols. H_2O, forms small, well-formed crystals; and the *lead* salt is anhydrous. The *diazonaphthalenesulphonic acid* is obtained as a green microcrystalline powder, and when boiled with concentrated hydrochloric acid yields a chloronaphthalenesulphonic acid, from which, on treatment of its potassium salt with phosphorus pentachloride, a dichloronaphthalene (probably 1′ : 2) is obtained, melting at 48°.

W. P. W.

Action of Phosphorus Pentachloride on α-Hydroxynaphthoïc Acid. By R. Wolffenstein (*Ber.*, **20**, 1966—1967).—*α-Chlorocarboxylnaphthylorthophosphoric dichloride*, $POCl_2{\cdot}O{\cdot}C_{10}H_6{\cdot}CCl_3$, is obtained by warming α-hydroxynaphthoïc acid with phosphorus pentachloride (rather more than 2 mols.) in presence of a little phosphoric chloride, until the mixture is homogeneous. The product, when cold, is poured on to ice. It crystallises from light petroleum in transparent, colourless prisms melting at 115°. The compound is analogous to that obtained by Anschütz and More (*Annalen*, **239**, 314) from salicylic acid and phosphorus pentachloride.

N. H. M.

Indoles from α-Naphthylhydrazine. By A. Schlieper (*Annalen*, **239**, 229—239).—The indoles from α-naphthylhydrazine are prepared by the same methods which the author employed in the preparation of the β-naphthindoles (this vol., p. 554).

α-Naphthylhydrazinepyruvic acid has been previously described by E. Fischer (Abstr., 1886, 554). The *ethylic* salt forms yellow prisms, and is freely soluble in benzene, chloroform, ether, acetic acid, and hot alcohol. It melts at 100°, and on fusion with zinc chloride yields ethyl α-naphthindolecarboxylate and small quantities of indole and α-naphthindolecarboxylic acid. *Ethyl α-naphthindolecarboxylate* can be distilled in a current of superheated steam. It melts at 170°, and dissolves freely in benzene, hot alcohol, and glacial acetic acid.

α-Naphthindolecarboxylic acid, $C_{10}H_6{<}\begin{matrix}NH\\CH\end{matrix}{>}C{\cdot}COOH$, melts at 202°, and decomposes at 210—220°, yielding α-naphthindole; it is soluble in alcohol, ether, and acetic acid, and in alkalis. It is reprecipitated from the alkaline solution on the addition of an acid, and from the

ammoniacal solution on boiling. The nickel, cadmium, barium, and sodium salts are crystalline.

α-Naphthindole melts at 175°, and dissolves freely in alcohol, ether, and benzene. It is less soluble in hot water, dilute acetic acid, and light petroleum, and it is deposited from these solutions in colourless plates. The *picrate* crystallises in needles. The solution of the indole in acetic acid gives a red coloration with strong nitric acid, a colourless precipitate with hydrochloric acid, probably $(C_{12}H_9N)_2,HCl$, and a bluish-green precipitate on boiling with hydrogen peroxide.

α-Hydronaphthindole is obtained as a crystallisable oil on boiling the alcoholic solution of the indole with zinc-dust and hydrochloric acid. The alcoholic solution gives a red-violet coloration with silver nitrate, ferric chloride, and nitrous acid. The salts of the mineral acids are soluble in water. The oxalate is deposited from hot alcoholic solution in colourless needles melting at 166°. It is precipitated on adding oxalic acid to a solution of the base.

Methyl-α-naphthindole, $C_{10}H_6<\begin{matrix}NH\\CH\end{matrix}>CMe$, obtained from acetone-α-naphthylhydrazine (Abstr., 1886, 555), is soluble in alcohol, ether, benzene, acetic acid, and in hot water. It melts at 132°. The picrate is deposited from hot benzene in dark red needles, and melts at 167—168°. The acetic acid solution of the indole gives a cherry-red coloration with ferric chloride, and on the addition of water a coloured precipitate is formed. W. C. W.

Nitroacenaphthene. By E. Jandrier (*Compt. rend.*, **104**, 1858).—Nitric acid of sp. gr. 1·34 is added drop by drop to a warm saturated solution of acenaphthene in glacial acetic acid, and the product crystallised from alcohol, ether, or acetic acid. It forms white, silky needles which melt at 155°, and sublime at a low temperature, condensing in pale-yellow needles. The nitro-derivative is easily reduced by zinc and hydrochloric acid or iron and acetic acid, and the amido-derivative yields a blue-violet product when carefully oxidised. With potassium dichromate and sulphuric acid, or with calcium hypochlorite, it yields a green solution and a green precipitate. The diazo-derivative forms a yellow colouring matter with phenol, and scarlet and ponceaus with β-naphthol or its disulphonic acid. C. H. B.

Methylerythrohydroxyanthraquinone. By W. Birukoff (*Ber.*, **20**, 2068—2071).—Baeyer and Drewsen (Abstr., 1882, 1099) prepared methylerythrohydroxyanthraquinone [Me : OH = 1 : 4] in very small quantity by the condensation of phthalic anhydride and paracresol with sulphuric acid. A yield of 5 per cent. of the paracresol employed can be obtained if phthalic anhydride (5 parts) is heated with paracresol (2 parts) and sulphuric acid (15 parts) for 10 minutes at 160°. The compound crystallises in yellowish-red, or from acetic acid in dark-brown, glistening needles, melts at 169—170°, and readily sublimes. In alkalis, it dissolves with a red colour; ammonia and soda do not dissolve it in the cold, and only sparingly on boiling; and with barium oxide and lime it yields insoluble brick-red lakes. Fusion with potassium hydroxide converts it with difficulty into a

coloured hydroxyanthraquinone, whilst sulphuric acid dissolves it with an orange-yellow colour, and the solution gives a spectrum corresponding entirely with that of erythrohydroxyanthraquinone. The *acetyl*-derivative crystallises in yellow needles and melts at 179—180°.

α-Methylanthracene [Me = 1] is obtained on distilling methylerythrohydroxyanthraquinone with zinc-dust. It crystallises in white laminæ, melts at 199—200°, and is soluble in alcohol, yielding a solution fluorescing a pale blue. The *picrate* crystallises in red needles. When oxidised with chromic acid in acetic acid solution, it is converted into *α-methylanthraquinone*, together with the corresponding carboxylic acid if the reaction is allowed to become violent. The quinone crystallises in small, white needles, which speedily become pale-red on exposure to light; it melts at 166—167°, and is readily soluble in benzene and alcohol. W. P. W.

Preparation of Anthranol and Dianthryl. By C. Liebermann and A. Gimbel (*Ber.*, **20**, 1854—1855).—These two compounds can easily be prepared by the reduction of anthraquinone by tin and acetic acid. If 10 grams of anthraquinone is dissolved in 500 grams of boiling glacial acetic acid, 25 grams of zinc added, and then a few c.c. of fuming hydrochloric acid added from time to time, almost all the quinone is reduced to anthranol, $C_6H_4\begin{<}\begin{matrix}CH\text{—}\\ |\\ C(OH)\end{matrix}\end{>}C_6H_4$, which is then precipitated by pouring the solution into acidulated water. If, however, 10 grams of anthraquinone are added to just enough glacial acetic acid to form a thin paste, this then heated to boiling, 40 grams of tin added in two or three portions, and finally about half as much fuming hydrochloric acid as there was acetic acid, the reduction takes place almost entirely to dianthryl (dianthranyl), $C_{28}H_{18}$, a small quantity of anthracene being formed at the same time. *Dibromodianthryl* is obtained by the action of bromine on a carbon bisulphide solution of dianthryl. It forms pale yellow prisms which melt considerably above 300°. L. T. T.

Terpenes and Ethereal Oils. Part V. By O. Wallach (*Annalen*, **239**, 1—54). The eight isomeric terpenes may be distinguished from each other by comparing the properties of their compounds with HCl, HBr, HI, &c., as shown in the following table (p. 966.)

The compounds of the terpenes with 2 mols. HBr, HI, &c., may be conveniently prepared on the small scale by saturating glacial acetic acid with hydrogen chloride, and adding this solution to the terpene dissolved in acetic acid. When the product is poured into ice-cold water, the compound separates in the pure state.

The bromides are prepared by adding bromine to the terpene diluted with ten times its volume of glacial acetic acid. They are purified by recrystallisation from warm ethyl acetate. The hydrochlorides are easily decomposed by boiling with glacial acetic acid and anhydrous sodium acetate, the chief product being the original

	Pinene.	Camphene.	Limonene.	Dipentene.
$C_{10}H_{16}$ B. pt.	159—161°	160—161°	175°	180—182°
$C_{10}H_{16}$ M. pt.	—	48—49°	—	—
$C_{10}H_{16},HCl$ B. pt.	207—208	decomposes	—	—
$C_{10}H_{16},HCl$ M. pt.	about 125°	—	—	—
$C_{10}H_{16},HBr$. M. p.	90°	—	—	—
$C_{10}H_{16},2HCl$. ,,	—	—	[50]*	50°
$C_{10}H_{16},2HBr$. ,,	—	—	[64]*	64
$C_{10}H_{16},2HI$. ,,	—	—	[77 or 79°]*	77° or 79°
$C_{10}H_{16}Br_4$. ,,	—	—	104—105°	125°
$C_{10}H_{16}N_2O_3$. ,,	—	—	—	—
Colour with acetic anhydride and conc. H_2SO_4	pink or yellow	yellowish	red	red

	Sylvestrene.	Terpinolene.	Terpinene.	Phellandrene.
$C_{10}H_{16}$ B. pt.	175—178°	185—190°	180°	about 170°
$C_{10}H_{16}$ M. pt.	—	—	—	—
$C_{10}H_{16},HCl$ B. pt.	—	—	—	—
$C_{10}H_{16},HCl$ M. pt.	—	—	—	—
$C_{10}H_{16},HBr$. M. pt.	—	—	—	—
$C_{10}H_{16},2HCl$. ,,	72°	†	—	—
$C_{10}H_{16},2HBr$. ,,	72	†	—	—
$C_{10}H_{16},2HI$. ,,	65—72°	†	—	—
$C_{10}H_{16}Br_4$. ,,	135°	116°	—	—
$C_{10}H_{16}N_2O_3$. ,,	—	—	155°	94°
Colour with acetic anhydride and conc. H_2SO_4	blue	red	red	red

terpene. If pinene monohydrochloride is treated in this manner at 200° for four hours, it yields camphene. The conversion of pinene into dipentene, terpinolene, and terpinene, has been previously described (Abstr., 1885, 550, and 1886, 70). Pure pentene and all its derivatives are optically inactive. The dihydriodide, $C_{10}H_{16},2HI$, is deposited from light petroleum in two distinct forms, namely, in rhombic crystals [$a : b : = 0{\cdot}6644 : 1$], melting at 77°, and in monoclinic crystals [$a : b : c = 1{\cdot}0269 : 1 : 0{\cdot}92619$; $\beta = 49° 54'$], melting at 78—79°. Pure dipentene is converted into terpinene by treatment with alcoholic sulphuric, or hydrochloric acid.

Cineol, cajeputol, and eucalyptol are identical. This substance crystallises when it is cooled in a freezing mixture.

Terpinolene is obtained by boiling terpene hydrate, terpineol, or cineol, with dilute sulphuric or phosphoric acid. The melting point of the freshly prepared tetrabromide is 116°, but old specimens melt at about 112°. At the moment of fusion, a slight evolution of gas is perceptible. Solutions of the tetrabromide are optically inactive.

* Identical with the corresponding dipentene compounds.

† Probably identical with the corresponding dipentene compounds.

By the action of hydrochloric, hydrobromic, or hydriodic acids on terpinolene, the hydrochloride, hydrobromide, &c., of dipentene are formed. Pure sylvestrene hydrochloride is obtained by saturating Swedish oil of turpentine (b. p. 174—178°) diluted with ether with dry hydrogen chloride. After an interval of two days, the ether is distilled off, and the residue is poured into shallow dishes, when the hydrochloride slowly crystallises out. The operation should be carried out in winter. After recrystallisation from warm alcohol, the hydrochloride melts at 72°. It is less soluble in ether and in light petroleum than dipentene hydrochloride. The ethereal solution is powerfully dextrogyrate. Sylvestrene boils at 175—178°; an intense blue coloration is produced by adding a drop of strong sulphuric or nitric acid to a solution of the hydrocarbon in acetic anhydride. Sylvestrene regenerated from the hydrochloride is identical with the hydrocarbon present in Swedish oil of turpentine. It is dextrogyrate.

The hydrochloride, hydrobromide, and tetrabromide crystallise in the monoclinic system.

The hydrochloride forms plates, $a : b : c = 2{\cdot}0199 : 1 : 2{\cdot}7641$; $\beta = 76° 32\frac{1}{2}'$.

The hydrobromide also forms plates, $a : b : c = 1{\cdot}8887 : 1 : 2{\cdot}6937$; $\beta = 73° 14'$.

For the tetrabromide, $a : b : c = 1{\cdot}2166 : 1 : 1{\cdot}6581$; $\beta = 46° 9'$.

Terpinene is obtained by gradually adding 70 c.c. of strong sulphuric acid to two litres of oil of turpentine. The mixture is kept cool and is well shaken. After an interval of two days the acid is neutralised with soda, and the terpinene distilled over in a current of steam. Dipentene, phellandrene, and cineol also yield the same hydrocarbon.

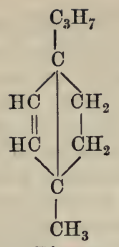
Terpinene nitrite, $C_{10}H_{16}{\cdot}N_2O_3$, is obtained in crystals by adding sodium nitrite in small quantities to a mixture of terpinene, acetic acid, and water. The compound is deposited in the course of two days at the ordinary temperature, or immediately in working on the small scale if the vessel containing the mixture is dipped for an instant into hot water.

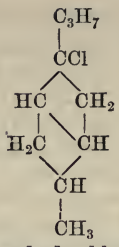
The nitrite melts at 155°. It is insoluble in water and light petroleum, but dissolves freely in alcohol, ether, and ethyl acetate.

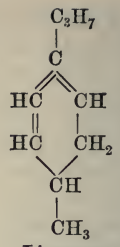
The solutions are optically inactive. The nitrite dissolves in strong hydrochloric, sulphuric, and acetic acids, and is reprecipitated unaltered on diluting the acid solutions. On reduction with stannous chloride, the nitrite is converted into a base which has not yet been properly investigated. Terpinine is not converted into camphene or any other terpene by treatment with alcoholic sulphuric acid, or strong sulphuric acid.

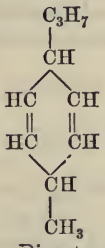
The properties of *phellandrene* have been recently described by Pesci (Abstr., 1886, 1038). The aqueous solution is dextrogyrate, but the nitrite is lævogyrate. The nitrite behaves like a saturated compound, and does not destroy the colour of bromine-water. Phellandrene has not been obtained in a pure state. It easily changes into dipentene- or terpinene-derivatives.

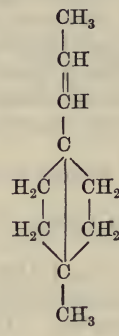
The author proposes the following formulæ for the terpenes—


Pinene.


Pinene hydrochloride.


Limonene.


Dipentene.


Phellandrene.

W. C. W.

Conversion of Dextrorotatory Terpene from Russian Turpentine by means of Hydratation and Dehydratation. By F. Flawitzky (*Ber.*, **20**, 1956—1965).—The dextrorotatory terpene employed was prepared from steam-distilled Russian turpentine by fractional distillation and treatment with dry potash; it was then warmed with sodium. It boils at 155·5—156·5° (corr.), sp. gr. = 0·8764 at 0° and 0·8600 at 20° (water at 4° = 1). Coefficient of expansion between 0° and 20° = 0·00095. At 20° (with 100 mm.) $[\alpha]_D = +27{\cdot}5$. $[\alpha]_D = \frac{+27{\cdot}5}{0{\cdot}8600} = +32{\cdot}0°$. Molecular refraction = 71·24. The terpene was treated with twice its weight of a mixture of 3 parts 90 per cent. alcohol and 1 part sulphuric acid of sp. gr. = 1·64. After six days, the solution was separated from the unchanged terpene, decomposed by water (kept cool with ice), and the portion which separated washed first with water, then with alkali. The product, when dried over potash, showed rotation (with 100 mm.) $[\alpha]_D = +35{\cdot}6°$; that is 8·1° more than in the case of the original terpene. The product precipitated from the solution dissolved in alcoholic sulphuric acid only to the extent of one half; when steam distilled, it gave three distillates having different rotatory powers. A substance boiling at 213·7° to 217·7° was obtained. $[\alpha]_D = +44{\cdot}5$ at 19·5° (with 100 mm.). Analysis showed it to be a hydrate, $C_{10}H_{16},H_2O$. It forms a thick liquid, insoluble in water, miscible with alcoholic sulphuric acid, and has a peculiar odour and a bitter burning taste. Sp. gr. = 0·9335 at 0° and 0·9189 at 19·5°.

Coefficient of expansion = 0·00081. $[\alpha]_D = +48·4$. Molecular refractive power = 77·28. A table is given showing the similarity between the dextro- and lævo-terpene hydrates. When the hydrate is saturated with hydrogen chloride, the *hydrochloride* $C_{10}H_{16}(HCl)_2$ is formed; this crystallises from alcohol in tabular crystals melting at 49·5°.

The fraction of the substance of the rotatory power $[\alpha]_D = +35·6°$, which boiled below 210°, gave $[\alpha]_D = +40·0°$. When purified by repeated distillation over sodium, it boiled at 173—176°, and crystals separate on cooling it to −25°. After being again distilled, it was pure. $[\alpha]_D = +49·1$ at 15°. Sp. gr. = 0·8627 at 6° and 0·8480 at 20°. Coefficient of expansion = 0·00089. $[\alpha]_D = +57·6$. It differs, therefore, distinctly from the original terpene, but resembles lævo-isoterpene, and is, therefore, described as *dextro-isoterpene*.

The new dextro-isoterpene resembles the dextro-isoterpene from oil of lemon in its molecular refraction and other physical properties. When the new isoterpene is saturated with hydrogen chloride, it becomes heated, but no crystalline hydrochloride separates. The *dihydrochloride*, $C_{10}H_{16}(HCl)_2$, is obtained by saturating the solution of the terpene in glacial acetic acid with hydrochloric acid, and adding water; it separates from alcohol in crystals melting at 49°.

N. H. M.

Action of Glacial Acetic Acid on Lævogyrate Camphene. By J. Lafont (*Compt. rend.*, **104**, 1717—1719).—Lævogyrate camphene, obtained by the action of alcoholic potassium acetate at 150° on terebenthene hydrochloride, was heated with 1·5 parts of glacial acetic acid in sealed tubes at 100° for about 60 hours. The product was then distilled in a vacuum, and the portion boiling above 100° was again treated in the same way, this process being repeated six times. The final product was washed with water and fractionated in a vacuum. The fraction boiling at 155—158° under normal pressure consists of non-combined camphene, the rotatory power of which has diminished to $[\alpha]_D = -19° 53'$. It yields a hydrochloride with a rotatory power $[\alpha]_D = +9° 32'$.

The fraction boiling at 125—127° under a pressure of 35 mm. consists of a dextrogyrate acetate, which is liquid at the ordinary temperature, but becomes pasty at −50°; sp. gr. at 0° = 1·002; rotatory power $[\alpha]_D = +19° 41'$. If heated with alcoholic potash in sealed tubes, it yields borneol, which when purified by sublimation melts at 211°. Its rotatory power is $[\alpha]_D = +14° 51'$; when treated with nitric acid, it yields a camphor which melts at 175°, and has a rotatory power $[\alpha]_D = -20° 2'$.

The action of acetic acid on lævogyrate camphene yields only one acetate, which is dextrogyrate, and when this is treated with alcoholic potash it yields potassium acetate and camphenol only.

C. H. B.

Black Pepper Oil. By L. A. Eberhardt (*Arch. Pharm.* [3], **25**, 515—519).—The oil had a specific gravity of 0·87352 at 15°, and showed a greenish colour, due neither to chlorophyll nor to copper. At 22°, the oil had a lævorotatory power of 3·2° in a column 100 mm. long. On rectification, a very small quantity passed over at 160°. Fractions obtained at 170°, 176°, and 180° were colourless; 190° faint

green; 250° green; 310° brown-green. Above 310°, a brown tenacious residue was obtained in which phenol could not be detected.

The 170° fraction, when rectified under reduced pressure, gave a terpene boiling at 164—165°, and showed a left-handed rotation of 7·6° in 100 mm.; it gave numbers agreeing with the formula $C_{10}H_{16}$, and a vapour-density of 480° by Hofmann's method. The composition of the other fractions was much the same as this. The terpene hydrate was obtained by Tilden's method (this Journ., 1878, 247). The tetrabromide was also obtained in well-crystallised forms. The oil consists of a lævorotatory terpene and isomeric compounds of higher boiling points. J. T.

β-Chloronitro-camphor. By P. Cazeneuve (*Bull. Soc. Chim.*, **47**, 926—927).—The β-chloronitro-camphor previously described (Abstr., 1884, 1041) is more readily soluble in alcohol than the α-compound, and may, therefore, be separated from its isomeride by washing the mixture with 80 per cent. alcohol. On spontaneous evaporation, the solution obtained deposits microscopic crystals which may be purified by repeated recrystallisation from 93 per cent. alcohol. Thus obtained it is a soft camphor-like substance, crystallising in microscopic arborescent forms; it softens at 91°, and melts at 98°; it is dextrorotatory, an examination of its alcoholic solution showing it to have the rotatory power $[\alpha]_j = +10{\cdot}5°$. The chlorine in this compound is much less stable than in its isomeride, as alkalis decompose it at the normal temperature, metallic chlorides and nitro-camphors being formed. Sodium ethoxide also attacks it, sodium chloride, and what appears to be an ethyl ether of a nitro-camphor, being formed. A copper-zinc couple also decomposes it, nitro-camphor being produced. The α-compound yields the same reactions, but only on prolonged boiling; the nitro-camphors formed are, however, the same in each case. A. P.

Strophanthus and Strophanthin. By A. W. Gerrard (*Pharm. J. Trans.* [3], **17**, 923; comp. this vol., p. 991).—Boiling alcohol completely removes both oil and extract from Strophanthus seed at one operation; the oil can then be easily poured from the extract, and adhering traces washed away with a little ether. The author was, like Elborne, unable to obtain any alkaloïd from the hairs of Strophantus seeds.

Strophanthin was prepared by dissolving the alcoholic extract, filtering, adding tannic acid in excess, and then collecting the precipitate, which after washing was mixed with basic lead acetate. The mixture was then dried, exhausted with warm alcohol, and filtered. Traces of lead were removed by hydrogen sulphide, and on evaporation *strophanthin* was obtained as a scaly residue, which was finally purified by solution in water and treatment with animal charcoal.

Strophanthin has well-marked glucosidal characters. The author was unable to obtain strophanthin in crystals as described by Fraser. R. R.

Cubebin. By E. Schär (*Arch. Pharm.* [3], **25**, 531—539).—Cubeb powder when extracted with ether yields a compound which

closely resembles aconitine and digitalin in its reactions, and also shows some resemblance to veratrine and morphine. This is probably cubebin, a non-nitrogenous, indifferent substance occurring crystallised in cubebs. Comparing cubebin and veratrine, the sulphuric acid test is most characteristic when the substances are dissolved in chloroform. On contact with concentrated sulphuric acid, cubebin gives at once an intense purple-red colour at the surface of contact, whilst veratrine passes through orange-yellow, yellowish-red, and blood-red to purple-red; also a characteristic fluorescence appears in the latter case. Cubebin, unlike veratrine, gives no purple-cherry-red colour with concentrated hydrochloric acid, neither do cane-sugar and slightly diluted sulphuric acid give the very characteristic colour reaction of veratrine. Sulphuric acid containing 10 to 15 per cent. of water gives with cubebin after a longer or shorter time, according to the strength of the acid and the temperature, the beautiful red tint described by Grandeau as produced by digitalin with concentrated sulphuric acid. A little bromine added to the cubebin mixture produces sooner or later the strong blue-red coloration which has been considered as characteristic of digitalin. These two substances can be distinguished by their reactions with phosphomolybdic acid and with hydrochloric acid. The reactions of cubebin and aconitine are also compared and but slight differences were observed. The author hopes to investigate further. J. T.

Pterocarpin and Homopterocarpin from Sandal Wood. By Cazeneuve and Hugounenq (*Compt. rend.*, **104**, 1722—1725).—Powdered sandal wood is mixed with an equal weight of calcium hydroxide, moistened with water, dried on a sand-bath, and extracted with ether. The colouring matter and resins unite with the lime and form compounds insoluble in ether. The yellow ethereal solution is distilled to dryness, the residue dissolved in alcohol of 93°, and afterwards recrystallised from alcohol and finally from ether. The product is a mixture of pterocarpin and homopterocarpin, and these can be separated by means of carbon bisulphide, which dissolves the homopterocarpin. 1 kilo. of sandal wood yields about 5 grams of homopterocarpin and 1 gram of pterocarpin.

Pterocarpin, $C_{10}H_8O_3$, forms white lamellar crystals insoluble in water and in cold alcohol, but somewhat more soluble in the hot liquid, slightly soluble in ether, from which it crystallises in lamellæ, insoluble in carbon bisulphide in the cold but slightly soluble on heating; readily soluble in chloroform, from which it crystallises in large monoclinic prisms with lævohemihedral faces. When dissolved in chloroform, it has a lævorotatory power $[\alpha]_j = -211°$. When heated, it becomes pasty above 145°, and melts at 152° with slight decomposition. It has a neutral reaction, is insoluble in acids and in concentrated potash solution even when boiled, gives a green coloration with concentrated nitric acid, and is decomposed by fused potash with development of an odour of coumarin.

Homopterocarpin, $C_{12}H_{12}O_3$, has the same general properties as pterocarpin. It crystallises well in needles which are soluble in ether, chloroform, benzene, and carbon bisulphide. It is strongly lævogyrate, and when dissolved in chloroform has a rotatory power

$[\alpha]_j = -199°$. It softens at 70°, begins to melt at 82°, and is completely fused at 86°; solidification takes place very slowly. Concentrated potash solution has no action even at 200°, but with fused potash it yields carbonic anhydride and phloroglucol, and an odour of coumarin is perceptible. When homopterocarpin is heated with twice its weight of concentrated hydrochloric acid at 120° for ten hours, it yields a red-brown, lustrous product which seems to be resorcinol ether, $OH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}OH$. The supernatant acid has a yellow colour, and when the acid is expelled and the liquid mixed with ammonia a very fluorescent substance is obtained. Methyl chloride is also formed in this reaction. This result indicates that homopterocarpin contains the resorcinol-group with one or several methyl-groups. In its stability and general properties, it resembles the internal anhydrides of the benzene series, especially coumarin.

The compound now described as homopterocarpin was formerly called pterocarpin (*Bull. Soc. Chim.*, 1874). C. H. B.

Bitter Principle of Calamus Root. By A. Geuther (*Annalen*, **240**, 92—110).—The author has repeated the experiments of Thoms (Abstr., 1886, 895), and obtained the following results: (1) the acorin prepared by Thoms' method contains nitrogen; it is a mixture of ethereal oil, acid, and bitter principle. No sugar is formed when it is boiled with dilute alkali. (2) Thoms' acoretin is not a product of acorin but forms the bitter principle contained in that substance. Acoretin is not reduced by nascent hydrogen but remains unaltered. When calamus root is steam distilled, a distillate containing methyl alcohol is obtained. N. H. M.

Chlorophyll. By E. Schunck (*Proc. Roy. Soc.*, **42**, 184—188).—The author prepares compounds of phyllocyanin and carbonic anhydride. Carbonic anhydride passed through alcoholic phyllocyanin in the presence of ferrous hydrate gave no result. With copper oxide, a slight action took place. With zinc oxide, the colour of the phyllocyanin changes to bluish-green, exhibiting absorption-bands similar to those of phyllocyanin zinc acetate. On adding acid, it is decomposed into phyllocyanin and carbonic anhydride. The absorption-bands and general properties of phyllocyanin zinc-compounds resemble those of chlorophyll. In order to determine their relative stability, compounds of phyllocyanin with zinc, ferrous, and cupric acetates together with uncombined phyllocyanin and chlorophyll were exposed to air and daylight. The cupric compound was very stable, whilst the zinc-compound decomposed almost as easily as chlorophyll itself, the ferrous compound holding a position between the zinc-compound and uncombined phyllocyanin. On boiling phyllocyanin with aqueous potash and zinc-dust, and acidifying with acetic acid, a precipitate is obtained which dissolves in ether, giving absorption-bands similar to those of phyllocyanin zinc acetate, but moved further away from the red. Compounds having characteristic absorption-bands are also obtained by the action of hydrochloric acid and tin on phyllocyanin.
H. K. T.

Derivatives from α-Quinolinedisulphonic Acid. By W. La Coste and F. Valeur (*Ber.*, **20**, 1820—1827).—The author has already described (Abstr., 1886, 629) α-dihydroxyquinoline obtained from the above acid. The *hydrochloride*, $C_9NH_5(OH)_2,HCl + H_2O$, crystallises in plates, is soluble in water, and melts at 254—256°. The *platinochloride* form a yellow, crystalline precipitate; the *picrate* yellow needles, soluble in warm water and alcohol, and melting at 227—237°. The *dibenzoate*, $C_9NH_5(OBz)_2$, yields white needles which dissolve in alcohol, ether, &c., but not in water or alkalis; it melts at 130—134°.

The *monacetate* crystallises in white needles, soluble in alcohol, ether, and boiling water, and melting at 115—117°; no diaceto-compound could be obtained. *Methoxy-hydroxyquinoline*, $OH\cdot C_9NH_5\cdot OMe$, is formed by the action of methyl iodide on dihydroxyquinoline dissolved in alcoholic potash. It forms an unstable oil soluble in boiling water. The *hydrochloride* crystallises in anhydrous needles, which under water become converted into prisms containing 1 mol. H_2O; it is soluble in hot water, and melts at 255—259°. The *platinochloride* forms insoluble needles which decompose when heated with water. The *picrate* yields yellow needles soluble in boiling water, and melting at 221—226°. *Dimethoxyquinoline*, $C_9NH_5(OMe)_2$, is produced when methyl iodide is heated with a magma formed of dihydroxyquinoline, potash, and very little methyl alcohol. It forms an oil which is not volatile with steam. The *hydrochloride* is left as an oil on evaporating its aqueous solution, but may be obtained crystalline from ether; it melts at 262—266°. The *platinochloride* forms dark-red monoclinic crystals; the *picrate* broad, yellow needles melting at 102—104°; the *methiodide* pale-yellow crystals melting at 210—212°.

L. T. T.

Existence of two Series of 4-(Ana)substituted Derivatives of Quinoline. By E. Lellmann (*Ber.*, **20**, 2172—2177).—When quinoline (1 part) is sulphonated with fuming sulphuric acid (5 parts), containing 1 part of sulphuric anhydride dissolved in 2 parts of ordinary sulphuric acid, at temperatures rising by 20° intervals between 180° and 260°, the yield of anaquinolinesulphonic acid is found to gradually increase with the rise of temperature. After removal of the greater part of the orthoquinolinesulphonic acid by crystallisation, the ana-acid can readily be obtained by heating the mixed crystals of the later separations at 110°, when it effloresces and can be separated by means of a sieve from the crystals of the ortho-acid. The ana-acid prepared in this way is identical with that obtained by the author and Lange from metamidobenzenesulphonic acid by Skraup's reaction (this vol., p. 737), also with that obtained by La Coste and Valeur by sulphonating quinoline (this vol., p. 379), and erroneously described by them as anhydrous, but it differs from that prepared by Fischer and Riemerschmid by direct sulphonation (Abstr., 1883, 91).

Fusion with a large excess of potassium hydroxide converts the author's anaquinolinesulphonic acid into a mixture of hydroxy-and dihydroxy-quinoline. *Dihydroxyquinoline*, $C_9NH_5(OH)_2$, crystallises in large, glistening, greenish-brown needles, becomes brown at 260°, melts above 320°, and is soluble in all the ordinary solvents. It yields

a hydrochloride which crystallises in lustrous, yellow needles, and is decomposed by water, but it does not form a platinochloride. Hydroxyquinoline, $C_9NH_6{\cdot}OH$, forms small, silvery scales, becomes brown at 210°, melts at 224°, and on fusion with potassium hydroxide is partially converted into the foregoing dihydroxyquinoline; its *platinochloride*, $(C_9NH_7O)_2,H_2PtCl_6 + 4H_2O$, crystallises in long, broad, brittle needles. This hydroxyquinoline differs from those obtained by Skraup's reaction from ortho-, meta-, and para-amidophenol, but resembles, in its melting point and other properties, the so-called β-hydroxyquinoline prepared by Skraup from amidoquinoline (m. p. = 109—110°), formed by the reduction of the nitroquinoline (m. p. = 72°) isolated by Claus and Kramer from the product of the direct nitration of quinoline (Abstr., 1885, 908); it is probably identical also with Riemerschmid's hydroxyquinoline obtained by the fusion of his 4-quinolinesulphonic acid with soda (*Inaug. Dissert*; comp. Abstr., 1883, 91).

Rejecting the hypotheses (1) that the quinolinesulphonic acids prepared by Riemerschmid and himself differ only in the fact that the former is anhydrous and the latter hydrated, or (2) that Riemerschmid's acid contains the sulphonic group in some position other than 4, and that intramolecular change to the 4-position occurs during fusion, the author regards the two acids as isomeric 4-quinolinesulphonic acids, and ascribes their isomerism to a cause similar to that obtaining in the case of the 4-quinolinecarboxylic acids (this vol., p. 502). The formation of the same hydroxyquinoline from the two isomerides is accounted for by assuming that only one of the two (supposed) possible hydroxy-derivatives is stable at the high temperature, and that the unstable form undergoes changes into this during the fusion.

W. P. W.

Action of Aniline on Mixtures of Alliphatic Aldehydes. By W. v. Miller (*Ber.*, **20**, 1908—1911).—Extending his own and Doebner's (Abstr., 1884, 1375) and C. Beyer's (Abstr., 1886, 629) work, the author has studied the action of aniline on a mixture of isobutaldehyde and acetaldehyde in the presence of hydrochloric acid. The product contained quinaldine and α-isopropylquinoline, the latter corresponding with Doebner's description (this vol., p. 504). The two bases were separated by means of their platinochlorides, that of quinaldine being the less soluble.

L. T. T.

Action of Aniline on a Mixture of Acetaldehyde and Propaldehyde. By G. Rohde (*Ber.*, **20**, 1911—1915).—The author prepared *α-β-dimethylquinoline* by the action of aniline on tiglic aldehyde (Lieben and Zeisel, Abstr., 1886, 783). It crystallises in rhombic plates or prisms, melts at 66°, and boils at 255—260°. It is slightly soluble in water, readily in organic solvents. The platinochloride and picrate are both crystalline. Another quinoline base was formed in small quantity at the same time, but has not yet been identified. When a mixture of acetic and propionic aldehydes was used in place of tiglic aldehyde the same dimethylquinoline was formed, together with α-ethyl-β-methylquinoline and quinaldine.

When quinaldine is fused with benzil, an acridine *base* is formed.

It is crystalline, and melts at 173°. Dimethylquinoline under like treatment yields two other bases melting at 120° and 240° respectively, and now under investigation. L. T. T.

Action of Aniline on a Mixture of Propaldehyde and Methylal. By W. v. Miller and F. Kinkelin (*Ber.*, **20**, 1916—1918).—In this reaction, β-methylquinoline and α-ethyl-β-methylquinoline are formed. When formaldehyde is substituted for methylal, β-methylquinoline and γ-ethyl-β-methylquinoline are formed, but the yield is very small. Attempts to prepare quinoline by the action of aniline on a mixture of formic and acetic aldehydes were unsuccessful. L. T. T.

Condensation of Quinaldine with Aldehydes. By W. v. Miller (*Ber.*, **20**, 2041).—A note calling attention to the point brought out in the researches of the author's pupils (see following Abstracts), that the first product of the condensation of quinaldines with an aldehyde is an aldol-like compound, which, however, cannot be isolated in every case, owing to the readiness with which it loses the elements of a molecule of water and is converted into an unsaturated compound. W. P. W.

Action of Isobutaldehyde on Quinaldine. By J. C. A. Brunner (*Ber.*, **20**, 2041—2042).—When equal weights of quinaldine and zinc chloride are heated at 100° with twice the theoretical quantity of isobutaldehyde, condensation occurs, and the product, after washing with hot water and aqueous soda yields, on extraction with ether and evaporation of the ethereal solution, a crystalline base, and a reddish-yellow, oily mother-liquor. The base, $C_9NH_6{\cdot}CH_2{\cdot}CH(OH){\cdot}CHMe_2$, crystallises in snow-white, spherical aggregates of microscopic needles, melts at 93°, and is readily soluble in ether, benzene, and alcohol, soluble in light petroleum and hot water. The salts formed with mineral acids are syrups, which can only be crystallised with much difficulty, and are readily soluble in alcohol; the *picrate*, $C_{20}H_{10}N_4O_7$, forms small, prismatic crystals belonging to the triclinic system, melts at 143—145°, and decomposes at 150°. W. P. W.

Action of Paraldehyde on Quinaldine. By F. Eisele (*Ber.*, **20**, 2043).—*α-Allylquinoline*, $C_9NH_6{\cdot}CH : CHMe$, [$C_2H_2Me = 2'$], is obtained when equimolecular proportions of quinaldine and paraldehyde are heated at 210° for four to five hours, and on distillation of the product after separation of the accompanying water is found in the fraction 249—253°. During the distillation, water is formed, and this is considered to prove that the aldol-like compound,

$$C_9NH_6{\cdot}CH_2{\cdot}CHMe{\cdot}OH,$$

is also one of the products of the reaction. α-Allylquinoline yields a hydrochloride and sulphate crystallising in needles, and a *platinochloride*, $(C_{12}H_{11}N)_2,H_2PtCl_6$, which crystallises in small, yellow tablets, and is insoluble in alcohol. W. P. W.

Action of Furfuraldehyde on Quinaldine. By J. O. Srpek (*Ber.*, **20**, 2044—2045).—When furfuraldehyde and quinaldine in molecular proportion are heated for two hours at 100° with a small quantity of zinc chloride, and after removal of the unaltered quinaldine the product is extracted with dilute hydrochloric acid, and the solution subsequently neutralised, a base, $C_{15}H_{11}NO$, is obtained, which crystallises from light petroleum at first in tufts of needles, afterwards in rhombic tables, and becomes black on exposure to light. The *hydrochloride*, $C_{15}H_{11}NO,HCl$, crystallises in small, yellow needles, the *nitrate*, $C_{15}H_{11}NO,HNO_3$, in small needles, and the *sulphate*, $C_{15}H_{11}NO,H_2SO_4 + H_2O$, in small, reddish needles; the *platinochloride*, $(C_{15}H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, is a yellow crystalline compound, sparingly soluble in water and alcohol, and the *picrate*,

$$C_{15}H_{11}NO,C_6H_2(NO_3)_3\cdot OH,$$

crystallises in small yellow needles. W. P. W.

Action of Paranitrobenzaldehyde on Quinaldine. By W. Bulach (*Ber.*, **20**, 2046—2047).—An aldol-like base,

$$C_9NH_6\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2,$$

is obtained when paranitrobenzaldehyde and quinaldine in molecular proportion are heated at 120° for three hours. It crystallises from alcohol in white, silky needles, and melts at 160°. The *platinochloride*, $(C_{17}H_{14}N_2O_3)_2,H_2PtCl_6$, is a brick-red, crystalline precipitate; the *nitrate*, $C_{17}H_{14}N_2O_3,HNO_3$, forms white needles, and the *picrate* crystallises in yellow scales.

Paranitrobenzylidenequinaldine, $C_9NH_6\cdot CH : CH\cdot C_6H_4\cdot NO_2$, is formed when the preceding base is heated with acetic anhydride on a sand-bath for three hours; it crystallises in tufts of needles, melts at 164—165°, and is readily soluble in ether, chloroform, light petroleum, and hot alcohol. W. P. W.

Methylation of Indole. By E. Fischer and A. Steche (*Ber.*, **20**, 2199—2201).—In a previous communication (this vol., p. 588) the authors described a base, $C_{11}H_{13}N$, obtained by treating methylketole with methyl iodide; this base they considered probably might be a quinoline-derivative. In the present paper, this supposition is confirmed, as the base on treatment with tin and hydrochloric acid is converted into *dimethyltetrahydroquinoline*, $C_9NH_9Me_2$ [Me : Me = 1′ : 3′]. This boils at 239°. When treated with methyl iodide, it yields the quarternary ammonium iodide, $C_9NH_9Me_3I$, melting with decomposition at 250—251°. The yellow, crystalline picrate melts at 161—162°.

When methylketone is heated in alcoholic solution with excess of ethyl iodide for 15 hours on the water-bath, it is converted into ethylmethylketole and a base boiling at 255—257°, most probably *dihydroethyldimethylquinoline*, $C_9NH_6Me_2Et$ [Et : Me : Me = 1′ : 2′ : 3′]. Its methiodide melts at 189° (uncorr.).

Ethylmethylketole, C_8NH_5MeEt [Et : Me = 1′ : 2′], boils at 287—288°

under 752 mm. pressure; it colours pinewood red, gives a dark-red picrate, and is insoluble in dilute acids.

Benzyl chloride also reacts with methylketole to form a quinoline base, but the yield is very small. Benzal chloride and benzotrichloride behave quite differently, the former acting like benzaldehyde (this vol., p. 265), the latter like benzoic chloride (this vol., p. 583).

1′-Methylindole is scarcely attacked by methyl iodide at 100°, but on heating the mixture for 12 hours at 120°, a good yield is obtained of a base, which probably is methyldihydroquinoline, C_9NH_8Me [Me = 1′].

A. J. G.

Derivatives of Pseudocarbostyril. By P. Friedländer and F. Müller (*Ber.*, **20**, 2009—2017; compare Abstr., 1885, 989).—*Methylpseudocarbostyril* is obtained when a solution of carbostyril in 12 parts of alcohol and so much water that the hot solution remains clear is mixed with a slight excess of methyl iodide and the whole boiled in a reflux apparatus, a concentrated aqueous solution of sodium hydroxide (1 mol.) being gradually added. The alcohol is distilled off, the residue treated with soda and extracted with chloroform. It crystallises from light petroleum in slender, white needles melting at 71·5°, readily soluble in acetone, alcohol, and chloroform. The *platinochloride*, $(C_{10}H_9NO)_2,H_2PtCl_6 + 2H_2O$, is sparingly soluble; the *mercurichloride*, $C_{10}H_9NO,HgCl_2$, crystallises from water in small, lustrous prisms melting at 189°. When methylcarbostyril is reduced by means of sodium in alcoholic solution, methylhydroquinoline is formed. When oxidised with potassium permanganate, a compound is obtained, which yields methylamine and an acid when boiled with baryta-water. Sodium amalgam converts methylpseudocarbostyril into a *compound*, $C_{10}H_{10}NO$, crystallising in small, lustrous plates which melt at 275—276°, and what is probably methylhydrocarbostyril, $C_{10}H_{11}NO$. In like manner, carbostyril is converted into hydrocarbostyril and a sparingly soluble *compound*, C_9H_8NO, which melts above 300°. This behaviour is analogous to that of ethoxycarbostyril (*Ber.*, **15**, 336 and 1424), which yielded on reduction two compounds, a lactim ether and a solid non-volatile compound, to which the formula of a dihydroethylcarbostyril, $C_{11}H_{13}NO$, was ascribed. The analyses agree, however, better with the formula $C_{11}H_{12}NO$. When warmed with hydrochloric acid, it yields a compound identical with the product of reduction of carbostyril. The sparing solubility, high melting point, and indifferent behaviour of these reduction products, make it probable that two or more molecules have united.

γ-Chloromethylpseudocarbostyril, C_7NH_5MeOCl [Me : O : Cl = 1′ : 3′ : 4′], is obtained from γ-chlorocarbostyril in a manner similar to methylpseudocarbostyril. It crystallises from methyl alcohol in hair-like needles which melt at 117·5°, dissolve readily in benzene, alcohol, acetone and chloroform, &c., sparingly in water and in light petroleum. It resembles methylpseudocarbostyril. When treated with alcoholic soda solution, the chlorine is readily displaced by methoxyl or ethoxyl.

γ-Methoxymethylpseudocarbostyril, $C_7NH_5MeON{\cdot}OMe$ [OMe = 4′], crystallises from dilute alcohol in slender, white needles which melt at 68°, and dissolve readily in alcohol, benzene, chloroform, and hot water;

it has stronger basic properties than methylpseudocarbostyril, and yields a sparingly soluble *hydrochloride*; the *platinochloride*,

$$(C_{12}H_{11}NO_2)_2,H_2PtCl_6,$$

crystallises in long pyramids. The *γ-ethoxy-compound* crystallises from water in slender, white needles which melt at 87·5°. When heated with hydrochloric acid at 120°, both alkoxy-derivatives yield a *compound*, $C_9NH_6MeO_2$, which crystallises in white needles melting at 259—260°; it is soluble in the usual solvents, and in caustic alkalis, from which it is precipitated by carbonic anhydride. It has the constitution $C_6H_4<^{C(OH):CH}_{-NMe\cdot CO-}>$, or $C_6H_4<^{CO\cdot CH_2}_{NMe\cdot CO}>$. When treated with nitrous acid, a sparingly soluble nitroso-derivative, $C_{10}H_8NO_2\cdot NO$, is formed. This crystallises from acetic acid in red needles which decompose at about 188°, dissolve in alkaline carbonates with green coloration, and yield methylpseudoisatin when heated with hydrochloric acid at 120°. Stannous chloride reduces it to *β-γ-dihydroxymethylpseudocarbostyril*; this crystallises from alcohol in sparingly soluble needles which decompose at 210°. When a drop of soda is added to the alcoholic solution, a greenish-blue precipitate is formed which gradually dissolves with yellow colour; on adding ferric chloride, it acquires an emerald-green colour, which changes to reddish-yellow on warming, and it then contains a *pseudoquinisatin*, $C_6H_4<^{-CO\cdot CO-}_{NMe\cdot CO}>$. The latter is very readily soluble in the usual solvents, dissolves in alkalis with yellow coloration, and melts at about 120—122°. N. H. M.

α-Metanitrophenylparamethoxyquinoline and its Derivatives. By W. v. Miller and F. Kinkelin (*Ber.*, **20**, 1919—1927). —*α-Metanitrophenylparamethoxyquinoline*, $C_9NH_5(OMe)\cdot C_6H_4\cdot NO_2$ [$C_6H_4\cdot NO_2 : OMe = 2' : 4'$], was prepared by treating a mixure of metanitrocinnamaldehyde and paranisidine with hydrochloric acid. It crystallises in glistening yellowish needles, melts at 130°, and is soluble in benzene, sparingly so in ether. Its salts are decomposed by water and their alcoholic solutions are not fluorescent. The *chloride* and *platinochloride* crystallise in needles. When the nitro-compound is reduced with stannous chloride, it yields *α-metamidophenylparamethoxyquinoline*, which crystallises in colourless iridescent needles, melts at 127°, and is soluble in ether and benzene, sparingly so in alcohol and boiling water. It forms three series of salts, acid, normal, and basic. The *sulphate*, $C_{16}H_{14}N_2O,H_2SO_4 + 2H_2O$, crystallises in concentrically grouped yellow needles; the *hydrochloride*, $C_{16}H_{14}N_2O,2HCl + H_2O$ in yellow prisms, and the *platinochloride*, $C_{16}H_{14}N_2O,H_2PtCl_6 + H_2O$, in thin, glistening prisms. *α-Metamidophenylparamethoxyhydroquinoline* is obtained from the amido-derivative by the action of tin and hydrochloric acid. It forms crystals melting at 87°. The *hydrochloride* forms compact plates; the *platinochloride* a brown, amorphous precipitate.

α-Metahydroxyphenylparamethoxyquinoline is obtained by diazotising the amido-base. It crystallises in scales, is soluble in alcohol, melts

at 188°, and forms compounds with alkalis. The *hydrochloride* and *sulphate* form yellow crystals, and the acid solutions are not fluorescent. When a dilute sulphuric solution is treated with chlorine-water, the precipitate formed redissolved by the addition of soda. and ammonia added immediately, this base shows the green coloration hitherto considered characteristic of quinine, and this coloration becomes more marked on further dilution with water. The amido-base does not show this reaction, the nitro-base but very slightly. *α-Meta-hydroxyphenylparamethoxyhydroquinoline* is formed from the hydroxy-base by the action of tin and hydrochloric acid. It crystallises in plates melting at 110—111°, and is easily soluble in alcohol and ether. The *hydrochloride* forms small plates, and gives an intense green coloration with ferric chloride. The *sulphate* and *sodium-derivative* are both crystalline.

The *α-* and *β-paramethoxydiquinolyline*, $C_{19}N_2H_{14}O$, were obtained by Skraup's reaction by heating the amido-base with glycerol, strong sulphuric acid, and nitro-phenol. The *α*-base is soluble in alcohol (but much less so than the *β*-base), ether, and benzene, sparingly in boiling water; it melts at 151°, but cannot be distilled without decomposition. Its ethereal solution shows blue fluorescence. Its salts are yellow; the *methiodide* is a yellow, crystalline powder. The *β*-base is easily soluble in benzene and alcohol, sparingly so in ether, and the two latter solutions show blue fluorescence. Its melting point is not definite. The *hydrochloride* and *platinochloride* are crystalline. These bases only show the green colour reaction, mentioned above, to a very slight extent. L. T. T.

Oxidation-products of Diquinoline [2′ : 2′]. By H. Weidel and J. Wilhelm (*Monatsh. Chem.*, **8**, 197—200; compare Abstr., 1886, 949 and 950).—In a former paper (Abstr., 1886, 950), the authors considered that all the evidence pointed to the constitutional formula of cyclothraustic acid being $C_9NH_6{\cdot}C(OH){:}N{\cdot}C_6H_4{\cdot}COOH$. They find, however, that when a mixture of anthranilic acid and quinaldine is heated, a substance is obtained which agrees in all respects with cyclothraustic acid, the constitution of which must therefore be $C_9NH_6{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, and consequently that of pyridanthrilic acid, $C_5NH_2(COOH)_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$. G. H. M.

Bases in Galician Petroleum. By F. X. Bandrowski (*Monatsh. Chem.*, **8**, 224—226).—The author has isolated a very small quantity of a base or series of bases from Galician petroleum. The substance gives all the reactions for and seems to belongs to the group of alkaloïds. G. H. M.

Occurrence of Alkaloïd-like Bases in Paraffin Oil. By A. Weller (*Ber.*, **20**, 2097—2099).—The so-called yellow oil of sp. gr. 0·850—0·860, obtained in the manufacture of Saxon petroleum, contains small quantities of basic substances, which can be separated by shaking with dilute sulphuric acid, precipitating with aqueous soda, and extracting with ether. A partial purification is then effected by redissolving and reprecipitating several times, and finally the dark-

brown product is subjected to steam-distillation to remove the non-volatile fluorescent impurities. The bases are thus obtained as a colourless oil, which is free from oxygen and sulphur, has an intensely unpleasant odour, and a sp. gr. = 0·98—0·99, does not solidify at −11°, and is readily soluble in alcohol, ether, and chloroform, very sparingly soluble in water. Bromine and methyl iodide react with the mixture of bases, and form non-crystalline products, and treatment with concentrated aqueous potash causes the evolution of strongly alkaline but ammonia-free vapours. A separation of the bases cannot be effected by repeated fractional distillation, since the product obtained after many distillations boils, like the oil, between 220° and 260°, without the thermometer remaining constant at any one point. The most characteristic salt described is the oxalate, which crystallises in scales, and is soluble in alcohol, chloroform, benzene, and light petroleum, sparingly soluble in ether and water.

W. P. W.

Normal Quinine Hydrochloride. By A. Clermont (*J. Pharm.* [5], **15**, 15).—A solution of the normal hydrochloride

$$C_{40}H_{24}N_2O_4,2HCl$$

is easily obtained, either by mixing equivalent solutions of normal quinine sulphate and barium chloride, or by adding an equivalent of hydrochloric acid to a solution of basic quinine hydrochloride. The solution obtained by either process, when completely evaporated below 100°, yields the normal hydrochloride. This salt dissolves easily in its own weight of water at the ordinary temperature, and appears to be suitable for hypodermic injections, as its solution is not caustic. Below 5°, it becomes a mass of crystals, which again liquefy at 15°.

J. T.

Amorphous Cocaïne. By R. Stockman (*Pharm. J. Trans.* [3], **17**, 861).—From the properties and reactions of amorphous cocaïne, it is concluded that the substance really consists of ordinary crystalline cocaïne retained in the amorphous state by *hygrine*, the liquid alkaloïd which is also present in cocaïne leaves. R. R.

Emetine. By H. Kunz (*Arch. Pharm.* [3], **25**, 461—479).—Ipecacuanha powder was extracted with ether until all soluble matter was removed. The dried powder was then treated with strong alcohol, and the tincture thus obtained freed from spirit by distillation. The dry residue was freed from tannic acid by the addition of 10 to 13 per cent. of ferric chloride in concentrated solution, and the addition of sodium carbonate to strong alkaline reaction, too much liquid being carefully avoided. The sodium carbonate sets free emetine, but not the tannic acid, and the former can be extracted by boiling with light petroleum. The author, however, finds it best to dry the mass on the water-bath, powder finely, and extract with hot alcohol. On distilling off the alcohol, the resulting impure emetine is dissolved in dilute sulphuric acid, fractionally precipitated by ammonia, and these precipitates are now dissolved in boiling light petroleum. From the saturated petroleum solution, the emetine separates

spontaneously on cooling or on passing a current of air, in the form of a snow-white amorphous powder. 10 kilos. of root gave 80 grams of pure emetine. The powder again dissolved in sulphuric acid, precipitated by ammonia, and taken up with light petroleum as above, gives a perfectly white, amorphous powder, highly electric, and quickly becoming yellow to brown in the light, soluble in alcohol to a wine-yellow solution. It is very sparingly soluble in cold water, but somewhat more soluble on heating. Light petroleum and ether dissolve only traces in the cold, but take up a large quantity when boiling. Methyl alcohol, chloroform, and benzene are also good solvents of emetine. The base has a decided alkaline reaction with litmus-paper. It fuses to a colourless liquid, which gradually passes through yellow to brown. The melting point appears to vary with the molecular condition and the state of dryness of the sample, from 65° to 74°. The formula seems to be $C_{30}H_{40}N_2O_5$. Emetine platinochloride, $C_{30}H_{40}N_2O_5,H_2PtCl_6$, is a whitish-yellow powder, unchanged in sunlight. Emetine appears to be, like quinine, a diatomic diamine. The chromate,

$$C_{30}H_{40}N_2O_5,H_2Cr_2O_7,$$

was also prepared. Emetine is insoluble in soda and potash, ammonia, and the corresponding carbonates. A methiodide, $C_{30}H_{40}MeN_2O_5I$, is readily formed, even in the cold.

Methylemetonium hydroxide, $C_{30}H_{40}MeN_2O_5{\cdot}OH$, is obtained by treating the iodide with silver oxide; it is strongly alkaline. Various salts of this base are described by the author. He further shows that emetine, like quinine, is probably a quinoline-derivative, and that the *Radix ipecacuanhæ* contains bilineurin or choline. J. T.

Alkaloïds of Gelsemium Root. By F. A. Thompson (*Pharm. J. Trans.* [3], **17**, 805—808).—The author has isolated a second alkaloïd, *gelseminine*, from the root of *Gelsemium sempervirens*.

Analyses of gelsemine and several of its salts point to the formula $C_{54}H_{69}N_4O_{12}$ (Gerrad considered it to be $C_{24}H_{28}N_2O_4$). It is tribasic. The following salts were analysed:—Hydrochloride, $C_{54}H_{69}N_4O_{12},3HCl$; aurochloride, $C_{54}H_{69}N_4O_{12},3HAuCl_4$; platinochloride,

$$2C_{54}H_{69}N_4O_{12},3H_2PtCl_6.$$

The nitrate and sulphate are also described, as are further several colour reactions for the alkaloïd.

Gelseminine could not be obtained in a state fit for analysis. It is a dark-brown resinous mass, permanent in air, sparingly soluble in water and light petroleum, readily so in alcohol, ether, and chloroform. It has strongly marked basic properties, but only amorphous salts have been obtained. Its reactions are described in detail.

A. J. G.

Asiminine. By J. U. Lloyd (*Arch. Pharm.* [3], **25**, 503).—The alkaloïd is obtained from the seed of *Asimina triloba* (Papaveraceæ) by extraction with alcohol, concentrating, and, to separate the fatty oil, diluting with water, acidifying with acetic acid, shaking well, and filtering after 24 hours. Ammonia is added to the filtrate until only a slight precipitate results, and the still moist precipitate is shaken

with ether. The residue from evaporation of the ethereal extract is taken up with a little alcohol, and a slight excess of hydrochloric acid is added. With a concentrated solution, the whole mass becomes crystalline, whilst a dilute solution requires concentration. The hydrochloride thus obtained can be purified by recrystallisation from hot alcohol. The pure alkaloïd can be obtained by solution in water, precipitation by ammonia, and drying. It is white, amorphous, tasteless, and odourless; insoluble in water, easily soluble in alcohol and ether, less soluble in chloroform and benzene. Excepting the acetate and nitrate, its salts are easily crystallised. The hydrochloride is slightly soluble in water, the other salts are easily soluble, and have a bitter taste. Minute quantities give with nitric acid a carmine-red coloration, which quickly becomes purple-red, and can easily be mistaken for morphine. With sulphuric acid, asiminine effervesces and dissolves with a yellowish-green colour, gradually passing through yellowish-red to dark red. Hydrochloric acid after warming, and the addition of some sulphuric acid, produces a purple-red colour in the liquid. J. T.

Cholic Acid. By F. Mylius (*Ber.*, **20**, 1968—1989; compare this vol., p. 606).—Cholic acid is readily purified by recrystallisation from alcohol. The results of several analyses of the acid and of the silver salt point to the formula $C_{24}H_{40}O_5$ (compare Latschinoff, this vol., p. 682). It readily forms stable compounds with alcohols. The *compound* $C_{24}H_{40}O_5 + MeOH$ forms colourless tetrahedra; compounds with propyl and ethylene alcohols were also prepared. No double compound with acetone could be obtained. Cholamide (Hüfner, Abstr., 1879, 949) crystallises from water with 3 mols. H_2O; it melts at 130—140°, solidifies at 180°, and melts then at 228° without decomposition or loss of weight; when it is recrystallised from alcohol, it again has the low melting point. When cholic acid is heated, it appears to yield a mixture of different anhydrides. *Phenylmercaptan-dehydrocholic acid*, $C_{36}H_{44}O_4S_2$, is obtained by passing hydrogen chloride through a solution of dehydrocholic acid in phenyl mercaptan, and crystallises from alcohol in lustrous needles melting at 220°. It has acid properties; the *sodium salt* forms hair-like needles. *Phenylmercaptan-phenylhydrazine-dehydrocholic acid*,

$$COOH{\cdot}C_{23}H_{33}(N_2HPh)_2(SPh)_2,$$

melts at 210—220°; it is almost insoluble in alcohol and glacial acetic acid.

Bilianic acid is prepared by adding 20 grams of cholic acid (free from alcohol) to a mixture of 60 grams of sulphuric acid, 160 c.c. of water, and 40 grams of potassium dichromate. It is purified by means of the potassium salt. It has the formula $C_{24}H_{34}O_8$. The silver salt, $C_{24}H_{31}O_8Ag_3$, was analysed. The *hydroxylamine compound*, $C_{24}H_{36}N_2O_8$, crystallises in lustrous plates soluble in dilute alcohol; the *phenylhydrazine-derivative*, $C_{36}H_{46}N_4O_6$, is sparingly soluble.

When crude bilianic acid is boiled with baryta-water, the barium salt of isobilianic acid is formed; the latter is readily soluble in cold, almost insoluble in hot water.

The above results point to the following three formulæ for cholic acid, dehydrocholic acid, and bilianic acid respectively :—

$$COOH\cdot C_{20}H_{31}(CH_2\cdot OH)_2\cdot CH\cdot OH\,;\quad COOH\cdot C_{20}H_{31}(CHO)_2\cdot CO\,;$$
$$C_{19}H_{31}(CO)_2(COOH)_3.$$

Cholic acid does not contain an aromatic nucleus, and the readiness with which it is destroyed by oxidation makes it improbable that any other closed-chain nucleus is present. N. H. M.

Myohæmatin. By C. A. MacMunn (*Journ. Physiol.*, **8**, 51—65).—Myohæmatin can be obtained in solution by extracting the muscles which contain it with ether. As a result of osmotic phenomena, a muscle juice exudes, and floating above it is the ether which, if the muscles of pigeons be used, contains in solution a yellow lipochrome. The muscle juice itself is of a red colour, and gives the spectrum of modified myohæmatin, which is not altered by a stream of either oxygen or carbonic acid. The juice is acid in reaction, and contains various proteïds, in addition to the myohæmatin, and also creatin, which crystallises out on evaporation. W. D. H.

Physiological Chemistry.

Sensitiveness of the Sense of Smell. By E. Fischer and F. Penzoldt (*Annalen*, **239**, 131—136).—The authors find that 1 vol. of mercaptan vapour in 50,000,000,000 vols. of air is clearly perceptible to the sense of smell, and 1 vol. of chlorophenol in 1,000,000,000 of air; or it is possible to detect by their odour $\frac{1}{4,000,000}$ mgrm. chlorophenol and $\frac{1}{400,000,000}$ mgrm. mercaptan. W. C. W.

New Constituent of Blood-serum. By L. C. Wooldridge (*Proc. Roy. Soc.*, **42**, 230—232).—A very small quantity of a proteïd substance, serum-fibrinogen, can be obtained by rendering undiluted serum distinctly acid by means of dilute acetic or sulphuric (4 per 1000) acid. It is constantly present in the serum of dog's and sheep's blood, but absent from that of the horse and ox. In physical characters, it resembles fibrin, but is more readily soluble in dilute alkali than that substance. It is totally different from paraglobulin, and is interesting in view of Schmidt's theory that two proteïds are necessary for coagulation; it was perhaps an admixture of this substance with paraglobulin that led Schmidt to suppose that the latter substance is one of the two necessary proteïds. On adding a solution of serum fibrinogen to peptone plasma, coagulation is brought about in a few minutes. After injecting it into the circulation, the shed blood remains uncoagulated for many hours. It has an extremely feeble influence on magnesium sulphate plasma, and hence contains but a trace of fibrin ferment. W. D. H.

Muscle Plasma. By W. D. Halliburton (*Proc. Roy. Soc.*, **42**, 400—401).—The facts described by Kühne relating to the properties of the muscle plasma of cold-blooded animals are true in great measure for that of mammals.

Admixture of muscle plasma with solutions of neutral salts prevents the coagulation of the latter. Dilution of such salted muscle plasma brings about coagulation; this occurs most readily at 37—40°. Saline extracts of rigid muscle differ from salted muscle plasma in being acid, but resemble it very closely in the way in which myosin can be made to separate from it; myosin in fact undergoes a recoagulation. This is not a simple precipitation; it is first a jellying through the liquid; the clot subsequently contracts, squeezing out a colourless fluid or salted muscle serum. This does not take place at 0°; it occurs most readily at the temperature of the body, and is hastened by the addition of a ferment prepared from muscle in the same way as Schmidt's ferment is prepared from blood. The ferment is not identical with fibrin ferment, as it does not hasten the coagulation of salted blood plasma; nor does the fibrin ferment hasten the coagulation of muscle plasma. The recoagulation of myosin is also accompanied by the formation of lactic acid.

The proteïds of muscle plasma are—1. Paramyosinogen, which is coagulated by heat at 47°. 2. Myosinogen, which is coagulated at 56°. It is on the presence of this proteïd that the power of fresh muscle juice to hasten the coagulation of blood plasma depends. 3. Myoglobulin, which differs chiefly from serum globulin in its coagulation temperature (63°). 4. Albumin, which is apparently identical with serum albumin α, coagulating at 73°. 5. Myo-albumose; this has the properties of deutero-albumose, and is identical or closely connected with the myosin ferment. The first two proteïds in the above list go to form the clot of myosin; paramyosinogen is, however, not essential for coagulation; the three last remain in the muscle serum.

Paramyosinogen, myosinogen, and myoglobulin are proteïds of the globulin class. They are all completely precipitated by saturation with magnesium sulphate, or sodium chloride, or by dialysing out the salts from their solutions. They can be separated by fractional heat coagulation, or by fractional saturation with neutral salts.

When muscle turns acid, as it does during *rigor mortis*, the pepsin which it contains is enabled to act, and at a suitable temperature (35—40°) albumoses and peptones are formed by a process of self-digestion. It is possible that the passing off of *rigor mortis*, which is apparently due to the reconversion of myosin into myosinogen, may be the first stage in the self-digestion of muscle. W. D. H.

Fermentation by Protoplasm from Recently Killed Animals. By Fokker (*Compt. rend.*, **104**, 1730—1732).—If a small quantity of any organ of a recently killed animal is taken, with all precautions to prevent access of bacteria, and is placed in a sterilised fluid and gently heated, it can convert sugar into acid and starch into glucose: but careful examination by means of the microscope and by cultivation, fails to show the presence of any microbes.

When an acid is produced, the change ceases after a short time, because the acid formed arrests the action of the protoplasm. If, however, the liquid is carefully neutralised, the change recommences, and will continue for several months if the liquid is kept neutral. The quantity of acid produced by the protoplasm is smaller than would be formed under the same conditions by the action of microbes. The difference between protoplasm from a healthy animal and microbes lies mainly in the tendency of the latter to multiply. The only alteration which the tissues undergo during the fermentative changes which they produce, is the destruction of the nucleus.

C. H. B.

Action of Caffeïne and Theïne on Voluntary Muscle. By T. L. Brunton and J. T. Cash (*Proc. Roy. Soc.*, **42**, 238—239).—Both caffeïne and theïne cause rigor in the voluntary muscles of frogs; in the same frog, the stronger the solution used the more powerful is the action; although a large dose will often cause less action in one frog than a smaller one will cause in another. Theïne is rather more powerful than caffeïne; theïne, moreover, tends to produce rhythmical contractions in the muscle. The addition of lactic acid or chloride of calcium aids, whilst potash diminishes the action of the alkaloïds. W. D. H.

Chemical Constitution and Physiological Action. By T. L. Brunton and J. T. Cash (*Proc. Roy. Soc.*, **42**, 240).—The distinctive action of the lower members of the fatty series is their stimulant and anæsthetic action on the nerve centres. The members of the aromatic series also affect the nervous system—especially the motor centres, producing convulsions and paralysis. Benzene, chlorobenzene, bromobenzene, and iodobenzene are similar in their action on frogs, the halogen radicles not modifying the action of the benzene to any great extent. The introduction of hydroxyl into the benzene nucleus intensifies the convulsant action. W. D. H.

Diabetes and Glycerols. By W. B. Ransom (*Journ. Physiol.*, **8**, 99—116).—The following conclusions are drawn from experiments on rabbits:—(1) That certain forms of glycosuria—for instance, that produced by puncture of the medulla oblongata, may be checked by glycerol; (2) that glycerol acts more efficiently when introduced into the alimentary canal than when injected subcutaneously; (3) that glycerol checks glycosuria by inhibiting the formation of sugar in the liver; (4) that in this way it may lead indirectly to an accumulation of glycogen in the liver. Viewing the formation both of glycogen and sugar as a process of cell metabolism, quite independent of ferment action, it is impossible to suppose that glycerol produces its effect by acting on a ferment in the blood, but more probably it exercises some direct influence on the protoplasm of the liver cells. The usual theory of a ferment which comes especially into play after death and changes the glycogen in the liver into sugar is considered untenable; and the *post-mortem* formation of sugar is regarded as being due to metabolism still going on in the cells of the liver which retain their vitality for some time after the heart has stopped.

W. D. H.

Lævorotatory β-Hydroxybutyric Acid in the Blood of a Diabetic Patient. By L. Hugounenq (*Bull. Soc. Chim.*, **47**, 545—546).—Lævorotatory β-oxybutyric acid has been recognised in the urine of diabetic patients; the author has now detected its presence in the blood. The process used for its identification was as follows:—The blood was kept in contact with ether until the sugar present had been removed; it was then evaporated to dryness on the water-bath, and the solid coagulum exhausted with boiling water; the extract was precipitated with basic lead acetate and ammonia, and the filtered solution examined in the polariscope when the presence of the acid was indicated by its lævorotatory action. A second portion of the blood was then taken, evaporated, and extracted with water as in the first case, the aqueous solution evaporated almost to dryness, and the product treated with an equal volume of sulphuric acid and distilled; on fractioning the distillate, and treating the fractions with a freezing mixture, crystals separated which, after recrystallising from ether, were recognised as crotonic acid by the melting point (70—71°), this acid having been formed by the dehydration of β-hydroxybutyric acid. According to the results obtained by Külz (who found the rotatory power of β-hydroxybutyric acid to be −23·4°), the author found the blood contained 4·27 grams of the acid per litre, the urine of the same patient containing 4·48 grams per litre. A. P.

Does Human Urine contain Free Acid? By E. Brücke (*Monatsh. Chem.*, **8**, 95—100).—The theory generally accepted of the cause of the acidity of urine is that it is due to the presence of the acid phosphate of sodium or potassium in that secretion. E. Salkowski (*Lehre vom Harn*, Berlin, 1882, 15) leaves the question open as to whether hippuric acid which is present in small amount, is free or combined. The present research consists of experiments with congo-red, the colour of which is changed by acids. One part of hippuric acid dissolved in 55,000 of distilled water free from ammonia, causes a solution of congo-red to become violet or inky in colour. Hippuric acid does not appear however to be present in urine, and no urine hitherto examined produces any change on congo-red.

If to a solution of that pigment, a few drops of dilute sulphuric, phosphoric, or hydrochoric acid be added, the liquid assumes an inky tint. If this mixture is dropped into urine, each drop becomes red again, or if the urine be first coloured with congo-red, and acid added drop by drop, the cloud caused by the first drops redissolves: so that one cannot use this method for titration. If more acid is added, a precipitate of a rust-red colour in which the pigment is fixed settles, and the urine can be filtered off having its normal colour. The use of congo-red paper is hardly more satisfactory. If the paper be coloured violet by phosphoric acid, it is found that a solution of sodium chloride will render it red. This cannot wholly depend on the unequal diffusion of acid and base. A solution of congo-red rendered violet by hydrochloric acid is also made red by sodium chloride: this is probably not due to a union of the sodium chloride with the acid, but perhaps to a raising of the refractive index of the mixture, and a molecular alteration of the pigment. The colour is

browner than that produced by acids. If the solution of the pigment and sodium chloride be added to urine, it dissolves with a bright red colour. These facts teach that the bases in urine are not so far saturated with acids that the addition of more acid necessarily involves the presence of free acid. Whether the bases are metallic or not must be ascertained by future investigation; urea certainly has no effect on a solution of the pigment rendered violet by acid.

Carbonic acid is also not free in the urine, for congo-red is easily affected by that acid. In certain circumstances, free uric acid is sometimes present in urine in a crystalline form; but in such urine congo-red also shows that there is no free uric acid in solution at the same time. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Reduction of Silver Salts by Living Protoplasm. By T. Bokorny (*Ann. Agronom.*, **13**, 239—240).—The blackening of argentic nitrate by the protoplasm of living cells, discovered some years ago by the author and Loew, has been attributed by Beaumann and Hoppe-Seyler to the action of hydrogen peroxide. The author finds, firstly, that hydrogen peroxide cannot be detected in the living cells of *Spirogyra* by any test, secondly, that dead cells of *Spirogyra* even after imbibing a 10 per cent. solution of hydrogen peroxide, will not effect the reduction. J. M. H. M.

Changes in the Proteïds of Seeds during Germination. By J. R. Green (*Proc. Roy. Soc.*, **41**, 466—469).—Gorup-Besanez (*Ber.*, 1874, 1478) stated that the changes in the reserve proteïd materials during germination are probably due to the action of a proteolytic ferment. This was disputed by Krauch (Abstr., 1878, 996). The present experiments demonstrate in the case of the seeds of the *Lupinus hirsutus*, the correctness of Gorup-Besanez' view. The seeds were allowed to germinate for about a week; they then gave an acid reaction to test-paper; the cotyledons were ground, extracted with glycerol, and the extract dialysed until no trace of any crystalline substances which had formed during the germination could be detected in the dialysate. No trace of peptone passed the dialyser even after a week's exposure. The extract was then acidified with hydrochloric acid to the extent of 0·2 per cent., put into a fresh dialyser, some swollen-up boiled fibrin added, and the dialyser surrounded with 0·2 per cent. hydrochloric acid, and exposed to a temperature of 40°. Control experiments with acid only, or with boiled digestive extract, were carried out side by side. Digestion was slow, but after some time the dialysate contained peptone and leucine, while in the control experiments there were no such substances. The proteïds of the seeds are changed by this ferment in the same way as fibrin is. The ferment exists in the resting seed as a zymogen,

which is easily convertible into the ferment: the resting seeds have moreover a neutral reaction. The ferment acts best in a slightly acid medium; its activity is hindered by neutral salts and destroyed by alkalis, and is most active at a temperature of 40°. The process of germination is started or accompanied by a transformation of the zymogen into ferment on the absorption of water, and the development of vegetable acids in the cells of the seed: the ferment so developed converts the proteïds of the resting seed into acid albumin or para-peptone, peptone, and crystalline amides. The nitrogen travels from the cells of the seed to the growing points in the form of amides, not in that of peptones or other proteïds. W. D. H.

Molecular Respiration of Plants. By N. W. Diakonoff (*Ann. Agronom.*, **13**, 229—233).—Experiments with the higher plants lead the author to the following generalisations which amplify those formerly arrived at from a study of intramolecular respiration amongst the moulds. The intensity of disengagement of carbonic anhydride by vegetable cells in the absence of the oxygen of the air is determined by the activity of the fermentative processes which take place in the cells. As soon as oxygen ceases to be supplied in quantities sufficient for normal respiration, fermentation sets in; with a renewed supply of pure oxygen, normal respiration again becomes possible. Without the chemical action of pure oxygen, or as alternative some process of fermentative change (which constitutes the sole means of satisfying the requirements of a living cell in a medium deprived of oxygen), there is no disengagement of carbonic anhydride, that is to say, there is no life. J. M. H. M.

Exhalation of Oxygen by Fleshy-leaved Plants in Absence of Carbonic Anhydride. By A. Mayer (*Landw. Versuchs-Stat.*, **34**, 127—143).—Former researches by the author (Abstr., 1876, i, 95; *Landw. Versuchs-Stat.*, **21**, 277; **30**, 217) have shown that under certain conditions oxygen is exhaled by the leaves of some plants in absence of carbonic anhydride. This is more especially the case with the Crassulaceæ, and it was found that *Bryophyllum calycimum* leaves which contain malates, after a period of darkness (during night) react acid, but this reaction during the day time becomes much less. Comments are here made on the author's own experiments, and on those of others (de Vries and Sachs) who have combated his conclusions. His experiments made since 1883 show that "acid leaves," during insolation in an atmosphere free from carbonic anhydride, yield more oxygen the richer they are in free acid; moreover the older leaves being more acid, yield more gas than younger leaves, which are more nearly neutral; also those Crassulaceæ which emit most oxygen, are more acid in the morning than other plants (compare *Bryophllum calycimum* with *C. arborescens*), and when the elimination of oxygen has ceased, it is found that the leaves are nearly neutral in reaction. The acid present is a malic acid which differs in some respects from ordinary malic acid, but the calcium salt is a true malate; this acid and the calcium salt diminish during insolation, just as if the whole consisted of free acid, the products produced

by the change being starch, sugar, &c., and the amount of oxygen which should be separated by the produced carbohydrates, agrees well with the quantity of oxygen found to be set free by insolation. From all these facts, the author has drawn the conclusion that the changes which occur as above are part and parcel of the regular assimilation in the plant, that is processes of reduction which take place in the green portions of the plant, and that the malic acid of the Crassulaceæ is to be considered as an intermediate product. Further results have also been obtained, for it was found that the acid in dead leaves was not altered by light, nor did oxalic acid suffer any reduction nor give off oxygen. As regards the formation of malic acid in the dark, it is evidently the result of decomposition. The remainder of the article is occupied by a defence of his own theory against the arguments and experiments of de Vries, Kraus, and Warburg.

E. W. P.

Relations between Inorganic Salts containing Nitrogen and Plants. By H. Molisch (*Monatsh. Chem.*, 8, 237—259).—The most important conclusions arrived at by the author are the following:—

Nitrates are generally distributed in the vegetable kingdom; they usually occur to a much greater extent in herbaceous than in woody growths.

Nitrites could not be found in any of the plants examined (which amounted to about 100) in spite of their frequent presence in the ground. Former statements on the so-called presence of nitrites in different plants are based on errors and incorrect interpretation of results.

Plants possess the power of reducing nitrites with surprising quickness as soon as assimilated, and this is evidently the reason why they are never found in plants. Nitrates, however, will remain for weeks or even months in the vegetable cells before they are destroyed.

In contrast to the nitrates, nitrites act injuriously on certain plants even when employed in comparatively dilute solutions (0·1—0·01 per cent.).

Plants, to which the nitrogen is offered not in the form of nitrates, but in the form of nitrites or ammonia, never contain nitrates. It, therefore, follows that neither nitrous acid or ammonia undergo oxidation to nitric acid in the vegetable organism.

Contrary to the statement of Berthelot and André, plants, with perhaps the exception of bacteria, have not the power of producing nitrates from nitrogenous compounds. All nitrates in plants originate from outside, and when they exceed the amount contained in the substratum in the plant, the excess can be simply explained by the storing up of the salt. E. Schulze's experiments with lupines (this vol., p. 859) afford additional evidence in favour of this view.

Diphenylamine dissolved in sulphuric acid serves very conveniently for the detection of nitrates under the microscope. In those cases, however, in which humin substances are quickly formed by the action of the sulphuric acid, the reaction is more or less checked.

The paper also contains some observations on the localised appearance of substances which turn guaiacum emulsion and potassium iodide and starch-paste blue.

G. H. M.

The Proteïds of the Seeds of Jequirity. By S. H. C. Martin (*Proc. Roy. Soc.*, 331—334).—Warden and Waddell ("Non-bacillar Nature of Abrus Poison," Calcutta, 1884) have given the name "abrin" to the poisonous principle of jequirity (*Abrus precatorius*). They showed also that abrin was closely allied to "plant albumin"), but did not enter into any details as to whether it consisted of one or more proteïds. The present examination relates to the kinds of proteïds present in the seed, and is preliminary to an investigation of their physiological action. The red cuticle was first removed by shaking the seeds with chloroform; the cuticle sinks in that liquid, and the yellow kernel powder is readily removed and dried by allowing the chloroform to evaporate. The powder was then extracted with 15 per cent. sodium chloride solution and filtered. The proteïds in the filtrate were separated: (1) by saturation with ammonium sulphate; (2) by saturation with sodium chloride and the subsequent addition of glacial acetic acid.

The former method is the best; it takes shorter time, and precipitates the proteïds more completely. The precipitated proteïds were redissolved in distilled water, and the solution dialysed; this caused a copious precipitate, which was collected, washed with boiled distilled water, and dried over sulphuric acid. The residue consisted of dark-brown scales, which consisted of globulin and colouring matter. All the globulin is not, however, precipitable by dialysis. Alcohol was therefore added to the liquid, which had been in the dialyser for seven days, to precipitate the remaining proteïds. After six to eight weeks, the globulin was rendered insoluble by this means; the precipitate was collected, dried, and treated with distilled water, which dissolved out a proteïd which was an albumose. There are thus two proteïds present; a globulin and an albumose. The globulin is coagulated by heat at 75—80° in a 10 per cent. magnesium sulphate solution, at 66—73° in a 10 per cent. sodium chloride solution. It does not become insoluble when the latter solution is placed in an incubator at 35—40° like vegetable myosins; it belongs to the class of vegetable paraglobulins (this vol., p. 507).

The albumose is soluble in cold or boiling distilled water. It is not precipitated by saturation with sodium chloride unless a large amount of glacial acetic or phosphoric acid is added also. It is readily precipitated by saturation with neutral ammonium sulphate. It is not precipitated by nitric acid unless its solution be nearly saturated with sodium chloride. It gives the biuret reaction. This phytalbumose is seen to be closely allied to Kühne and Chittenden's deutero-albumose, and is identical with the α-phytalbumose of papaw-juice (Abstr., 1886, 642). W. D. H.

Safrole. By — Flückiger (*J. Pharm. Trans.* [3], **17**, 989—990). —Safrole exists not only in the essential oil of sassafras root, but probably in other plants belonging to the natural order of *Lauraceæ*. In Germany, safrole is now extracted on a large scale from the oil of the camphor tree, *Cinnamomum camphora*. An odour resembling that of sassafras is noted in *C. Parthenoxylon*, *C. glanduliferum*, and in *Beilschmiedia obtusifolia*. Safrole is associated with eugenole in the

fruit of *Illicium religiosum*, and in *Illicium anisatum* it is replaced by anethole. The empirical formulæ of these three highly aromatic substances, $C_{10}H_{10}O_2$, $C_{10}H_{12}O_2$, and $C_{10}H_{12}O$, suggests that probably they are capable of being converted one into another. R. R.

Strophanthus. By W. Elborne (*Pharm. J. Trans.* [3], **17**, 743—747).—The seeds of *Strophanthus kombé* yield 20·8 per cent. of fixed oil when extracted with light petroleum; 0·9 per cent. of chlorophyll and fat when extracted with ether; 1·5 per cent. of a bitter glucoside to absolute alcohol; and an additional 2·9 per cent. of bitter glucoside to water. These solvents were made to act successively on the dried and powdered seeds. It is remarked that when the alcoholic solution is evaporated to dryness at a low temperature, and the residue dissolved in water and set aside for a few days, the product becomes far more toxic. The cause of this change has not yet been investigated, but in the method adopted by the natives of Eastern Africa in preparing their arrow-poison from the plant, advantage appears to be taken of this fact. Bitter principles from *Strophanthus* have been already described by Fraser, and by Hardy and Gallois under the names of "*strophantin*," "*strophanthin*," and "*strophanthidin*." The author was unable to extract any alkaloïd from the comose hair of the seeds. R. R.

Poisoning of Plants by Lithium Salts. By J. Gaunersdorfer (*Landw. Versuchs-Stat.*, **34**, 171—206).—Experiments have previously shown that lithium is a constant compound of the ash of some plants, and that it is stored in their leaves, but not in their roots, and they even collect it when the presence of lithium in the soil is scarcely to be detected. Various experimenters are here referred to, also the results obtained by them. The author records the results of experiments made by him on various plants, *Cicer arietinum*, *Vicia faba*, &c., with solutions of lithium chloride of different strengths, 1·1—0·066 per mille; the descriptions are given in full detail, and the following conclusions are drawn: lithium is a fairly constant but not essential constituent of certain plants, but for most plants, in relatively small quantities it is a poison, and produces evident disturbances in the plants. Lithium is deposited in the *fully grown* leaves, whilst the young leaves, buds, and reproductive organs, failing as they do in hardened fibre, are exempt from the action of lithium, which does not reach them. It is the action of transpiration which carries lithium upwards, but this element can move sideways through the hardened cell-walls. Those plants which do not naturally contain lithium will live healthily in a soil which contains but a small portion of lithium, but finally the whole of the lithium is carried into the leaves which, dropping off, denude the soil of the element referred to.

E. W. P.

Composition of some Leguminous Seeds. By R. Waage (*Bied. Centr.*, 1887, 394—395).

A comparison with blue and yellow lupines shows that the white and blue are nearly of equal value, whilst the yellow contains more nitrogenous and less carbonaceous matter.

	Whole lupins.	Red Sanderbsen.	Peluschken.
Water	16·52	15·38	15·8
Ash	2·89	2·96	3·06
Sand	0·09	0·13	0·05
Crude fat	5·42	0·15	1·13
„ fibre	12·71	5·31	5·35
Non-nitrogenous extract	39·96	51·96	52·50
Crude albumin	22·41	22·24	22·02
Albumen	20·84	19·63	21·09
Digestible albumin	95·63	94·90	88·80
Soluble legumin	12·84	11·42	10·89
Nutrient ratio	2·94	2·31	2·35

The effect of steeping in water to remove the bitter portion of the lupines is to remove a large portion of the ash, some of the non-nitrogenous and some of the albuminous matter.

The total loss of valuable material amounts to 7·65 per cent., of which 1·86 is albumin and 5·8 is non-nitrogenous. E. W. P.

Experiments on Potatoes at Harelaw in 1886. By Aitken (*Trans. Highland and Agric. Soc.*, 1887 [4], **19**, 215—237).—The general results of the Harelaw experiments are summed up by the author as follows:—

Unmanured Section, Residual Fertility.—Insoluble phosphates have left a larger available residue than soluble phosphates; the largest has been left by bone-meal. The phosphates which produce the greatest result during the previous rotation have left the least residue. Nitrate of soda alone exhausts the land very much, with other manures it exhausts it more than other nitrogenous manures. Sulphate of ammonia has left considerable residue, or at any rate has not exhausted the land so much as nitrate of soda. Horn-dust and dried blood have left no more for the potato crop than sulphate of ammonia; rape-dust has left more residue than the other nitrogenous manures. Both potassium sulphate and chloride have left a residue for the potato crop, but the chloride has left rather more than the sulphate. Peruvian guano has left the land in better condition for the growth of potatoes than either Ichaboe or fish guano. Low class superphosphate has left more residue than high class.

Manured Section, Immediate Fertility.—The manure applied to potato plots in 1886 gave the following results:—Mineral phosphates found to pass through a sieve of 120 wires per linear inch produced nearly as good results as dissolved phosphates; they were more active than bone-meal or pure dissolved bones. Sulphate of ammonia did better than nitrate of soda when no dung was used. Horn-dust and dried blood are not sufficiently active for potatoes when applied with the seed. Potassium salts are of great importance to potatoes, and there

is little difference between the sulphate and chloride. Ordinary superphosphate, 28 per cent. soluble, is better than richer ones. When the potato crop is insufficiently manured, not only is the produce less, but the proportion of small tubers is greater; potash is the most important ingredient for the production of large tubers. A well-balanced manure for raising a potato crop without dung should contain about equal parts potash, ammonia, and phosphoric acid. When applied with dung, half the potash may be used. Manure for potatoes should be within easy reach of the roots, but may be slow acting; dung appears to be the most appropriate manure, producing a crop with a large proportion of large tubers. With dung, nitrate of soda is better than sulphate of ammonia; without it, the sulphate of ammonia is best. Where much dung is used, potash salts may not be required. J. M. H. M.

Production of Nitrates in Arable Soil. By P. P. Dehérain (*Ann. Agronom.*, **13**, 241—261).—The present series of experiments was undertaken to determine the conditions under which different substances acting as manures nitrify in the soil. They were made with the nitrogenous black matter of soil, ammoniacal salts, oil-cakes, farmyard manure, and the black matter of farmyard manure, under varying conditions of moisture and for different periods of time; in some instances, the proportion of manure to soil, and the temperature, both varied. The quantities of nitrate formed in the various mixtures from time to time were determined as follows:—100 grams of the mixture were introduced into a litre flask, the quantity of water required to make it up to the mark measured into it, left in contact for several hours, and repeatedly shaken; then 700 to 800 c.c. were withdrawn and evaporated down to about 10 c.c., and the nitric oxide determined according to Schloesing's method by measurement of the gas.

Nitrogenous Black Matter of Soil.—The soil employed contained 0·160 per cent. organic nitrogen and 0·015 per cent. nitric acid (N_2O_5?). Quantities of 100 grams of this soil were placed in glass beakers and moistened with 5, 10, 15, 20, and 25 c.c. of water respectively, and all the beakers were placed together under a bell-glass, and the nitric acid formed determined after several periods up to 90 days. With the 5 per cent. of added water, there was no nitrification at the end of 56 days, but all the other mixtures had commenced to nitrify at the end of the first period. After 90 days, the quantity of nitrate formed in a tonne (1000 kilos.) of soil was 250 grams in that moistened with 5 per cent. of added water; 16 grams with 10 per cent. water; 270 grams with 15 per cent. water; 290 grams with 20 per cent. water; and 370 grams with 25 per cent. water—the nitric acid formed thus attaining a maximum in the most humid mixture. The greatest rate of nitrification observed was 1 gram nitrogen nitrified per day per tonne of soil. Supposing this rate to be maintained during the active life of a cereal crop, say 100 days, the nitrogen nitrified would amount to 300 to 400 kilos. per hectare, a quantity greatly in excess of the requirements of the crop.

Ammoniacal Salts.—Quantities of soil watered with various propor-

tions of ammonium sulphate were placed in identical conditions with plain soil freely exposed to the air.

Sulphate of ammonia in quantities equivalent to 0·030 gram and 0·010 gram nitrogen per 20 grams of soil far from increasing the quantity of nitrate formed greatly hindered the nitrification in the soil. In a saturated atmosphere, however, with the soil freely supplied with water, doses of sulphate of ammonia up to 0·100 gram nitrogen per 100 grams soil did not prevent nitrification, although the larger the doses employed the less nitrates were formed.

A series of experiments with sulphate of ammonia equivalent to 0·010 gram nitrogen per 100 grams soil, moistened with 5, 10, 15, 20, and 25 grams water, showed that with the smaller proportions of water nitrification was less than in the parallel experiments with plain soil; with the larger proportions of water, more nitrogen was nitrified, that of the ammoniacal salt undergoing oxidation as well as that of the organic matter of the soil, and at a much faster rate, so that, for example, the addition of 0·010 gram nitrogen as ammoniacal salt to 100 grams soil containing 0·160 gram organic nitrogen doubled the quantity of nitrate formed during the course of the experiments. Frequently as much as one-hundredth of the nitrogen added as ammoniacal salt was nitrified per diem, whilst the nitrogenous matter of the soil scarcely gave rise to one-thousandth of its weight of nitric acid in the same time. The whole of the sulphate of ammonia added as manure is probably nitrified in the course of a few months. Some of the nitrates at first formed disappear afterwards, more especially in the most humid mixtures, and this is attributed by the author to the slow growth of moulds.

Maize Cake.—The nitrogen of maize cake is nitrified more quickly than that of the organic matter of soil, more slowly than that of ammonium sulphate, so that if a mixture of the two is used as manure, when the action of the latter is exhausted that of the former still continues. The influence of humidity is the same as in the preceding cases.

Farmyard Manure.—2 per cent. of farmyard manure was added to the soil, corresponding to a dressing of 72 tonnes per hectare. Even with 5 per cent. of added water some degree of nitrification occurred, whereas with plain soil of the same humidity there was none. With the largest proportions of water, nitrification was very irregular, no more nitrate being formed after 90 days than after 26, and in some cases the nitrate formed was less than with plain soil. These irregularities are doubtless due to the growth of moulds, &c., of which the spores and mycelia abound in farmyard manure. In point of rapidity of nitrification, farmyard manure comes next to ammonium sulphate, and before maize cake and plain soil.

Black Matter of Farmyard Manure.—This was obtained by extracting decomposed farmyard manure with water, filtering, and evaporating the filtrate to dryness by exposure to air alone. It contained 3·5 per cent. of nitrogen, and was added to the soil in the proportion of 0·3 per cent., thus introducing the same quantity of nitrogen as that contained in the 0·050 gram ammonium sulphate used in a former series of experiments. With these mixtures, nitrification occurred

exactly as with plain soil, that is to say, the nitrogen of the black matter appeared to undergo no change. It appears to lose the capacity of being nitrified by the act of drying, since in trials with the *undried* extract of farmyard manure the nitrogen of the extract was nitrified in sensible quantities. J. M. H. M.

Free Phosphoric Acid and Superphosphates. By M. Weilandt (*Landw. Versuchs-Stat.*, **34**, 207—215).—Ritthausen has previously found that a solution of superphosphate and calcium carbonate produces dicalcium phosphate, and generally in the crystallised condition. The author has now studied the results of the reactions of a 10 per cent. solution of orthophosphoric acid on several alkaline carbonates. Pure barium and strontium carbonates produced 65·2 and 45·7 per cent. respectively of the insoluble phosphate, but when carbonic anhydride was passed in rather less of the bibasic and more of the monobasic phosphate and free acid were produced, as also many crystals. When, however, the concentration of the solution was raised, the results were reversed, but when the time of action was lengthened there was rather less of the bibasic salt produced, but in the filtrate was found a large conversion of the free acid into the monobasic salt. It would appear, then, that the crystallised phosphoric acid acts somewhat differently from the superphosphate.

The author, therefore, prepared a superphosphate from Mejillones guano and phosphoric acid, and with the solutions thus obtained he experimented on marble and other forms of carbonate, of which marl appeared to react most energetically. From the results obtained, it is evident that if superphosphate is applied to a well marled soil none will be lost by passing through unabsorbed in the monocalcium form, but all (98 per cent.) of the acid will be retained at the surface. As was to be expected, the more crystalline compounds are least readily acted on, whilst marl, which is readily decomposed, and in which the calcium carbonate is finely dispersed, becomes coated with the bibasic compound and prevents any further reaction. E. W. P.

Basic Cinder and other Finely-ground Insoluble Phosphates as Manures. By Aitken (*Trans. Highland and Agr. Soc.*, 1887 [4], **19**, 245—253).—The phosphates tried were Curaçoa phosphate with 87 per cent., Canadian phosphate with 59 per cent, Carolina phosphate with 57 per cent., Belgian phosphate with 40 per cent., and basic cinder with 40 per cent. of phosphate of lime. These were tried against each other and superphosphate of 28 per cent. at four different stations on turnips. It was found that only 40 to 50 per cent. of the ground Curaçoa, Carolina, Canadian, and Belgian phosphates would pass through a sieve of 120 wires per linear inch, whereas all the basic cinder passed through this sieve. A large sieve of this gauge was therefore made, and sufficient quantities of the mineral phosphates passed through it to try the sifted against the unsifted portions. Sulphate of ammonia and sulphate of potash were added in all cases to make a general manure, and quantities of the phosphates containing equal weights of phosphoric acid were employed. In almost all cases, the sifted phos-

phates produced a larger crop than the unsifted phosphates, amounting on an average to a gain of 1 to 1½ tons of roots per acre, and it seems reasonable to suppose that this increase would pay for the extra fineness of grinding. The superphosphate proved little if any superior to the sifted phosphates or the basic cinder, and this last phosphate appears to be at present the most finely ground as well as the cheapest in the market. The nature of the mineral phosphate used appears to be of much less importance than the fineness to which it is ground.

J. M. H. M.

Note by Abstractor.—The author says of basic cinder, "I do not doubt that its efficacy as a phosphatic manure is in the main to be attributed to the extraordinary fineness to which it is ground." No doubt fineness of grinding is extremely desirable, but the basic cinder appears to possess a distinct advantage over the mineral phosphates in the great relative solubility of the phosphate of lime contained in it. On some soils this tells very much; in the Downton experiments, conducted in 1885 by the Abstractor and another (this vol., p. 176), the coprolites were much more finely ground than the basic cinder employed, yet the latter produced far better crops than the former.

J. M. H. M.

Ground Felspar as a Potash Manure. By Aitken (*Trans. Highland and Agr. Soc.*, 1887 [4], **19**, 223—255).—The result of two small experiments, made at Pumphuston on turnips and at Boon on peas, is that felspar when ground so as to pass through a sieve of 120 meshes per linear inch undoubtedly acts as a potash manure. On the turnips, the felspar did better than an equivalent quantity of sulphate of potash, on the peas not so well. J. M. H. M.

Butter from various Districts. By E. Duclaux (*Compt. rend.*, **104**, 1727—1730).—The author has determined the proportion of volatile acids in various butters by the methods previously described. The butters examined were obtained from Isigny, Gournay, Brittany, and Cantal.

The ratio of butyric acid to caproic acid is practically constant in butter from the same district, but varies considerably from one district to another. In butter from Gournay, it is 1·6, Brittany 1·9, Isigny 2·1, Cantal 2·4. The total quantity of the two acids varies in different samples even from the same district. The production of butter of fine flavour and good quality is not simply a question of the method of preparation. C. H. B.

Analytical Chemistry.

Iodine Detection in Laminaria. By F. A. Flückiger (*Arch. Pharm.* [3], **25**, 519—522).—One decigram of the seaweed is ample for the detection of iodine. The weed in as small pieces as possible is mixed with twice its weight of not too fine pumice powder, boiled with water, and dried on the water-bath whilst being well stirred. The

mass is then roasted over a very gentle flame and extracted with 5 c.c. water in which the iodine can be detected by the addition of ferric chloride solution to acid reaction and shaking up with carbon bisulphide. Or a very dilute solution of chlorine-water may be used with one portion of the filtrate and ferric chloride with another.

J. T.

Iodimetric Studies: Application of the Method to the Analysis of Commercial Substances. By G. Topf (*Zeit. anal. Chem.*, **26**, 277—302. See this vol., p. 688).—Commercial sodium thiosulphate is nearly pure, and usually contains such minute traces of sodium carbonate that its titration by iodine is not affected thereby; nevertheless if present in larger quantity this salt would cause an error in the result equal to double its own amount, unless acidified iodine solution is used.

The iodimetric method serves well for the assay of commercial sodium sulphide. It is necessary to add the sulphide to an excess of acidified iodine solution, otherwise the alkali present induces oxidation of the sulphur, and causes the results to be too high.

Bunsen's explanation of the necessity for diluting sulphurous acid to 0·05 per cent. before titrating with iodine, namely, that above that strength a reverse action occurs, does not seem to be correct. Finkener has shown that with an excess of iodine the action is complete in a solution of any strength. Even sulphuric acid of 20 per cent. strength liberates no iodine from potassium iodide. Stronger acids are reduced, especially when much iodide is added, but up to 71 per cent. the product is hydrogen sulphide. Above that strength, sulphurous acid is also produced, but is not the sole product till 81 per cent. is reached. If Mohr's plan of neutralising the sulphurous acid before titrating it is adopted, it is still necessary to use an excess of iodine and to acidify before titrating back with thiosulphate.

In titrating stannous salts by iodine, the best results were obtained by adding tartaric acid and sodium hydrogen carbonate, then an excess of iodine, and then acid before titrating back. Zinc powder can be assayed by shaking it with excess of neutral iodine solution (in a bottle containing glass balls), and acidifying with acetic acid before titrating the excess.

In examining commercial iodine containing chlorine, it is necessary to dissolve in soda and add a small quantity of a sulphite to reduce the iodate formed by the action of the chlorine. A ferric salt and hydrochloric acid are then added and the iodine is distilled over into potassium iodide. The author figures a special distillation apparatus in which caoutchouc joints are avoided, and which gives excellent results. The same apparatus serves for the analysis of chlorates and hypochlorites by distillation with hydrochloric acid.

Diehl's method of titrating Weldon mud by digesting with potassium iodide and acetic acid and determining the liberated iodine is found to be a very practical one. Lead dioxide and red lead can be estimated in the same manner if sufficient sodium acetate is added to keep the lead iodide in solution. The results are more trustworthy than those obtained by distillation with hydrochloric acid. Nitrates,

which are often present in the commercial dioxide, are without influence.

Lastly, ferrous and ferric oxides, in hydrochloric acid solution, can be determined iodimetrically. For the ferrous oxide, a known excess of iodine is added (which may conveniently be done by adding potassium iodide and a standard solution of iodate), and then an excess of sodium acetate. The iron separates as basic ferric acetate and the residual iodine can either be distilled out, or after digestion at 60—70° in a stoppered bottle and cooling, can be titrated direct without filtering. For the ferric oxide, an excess of potassium iodide is added, and after digestion at 70° the liberated iodine is determined.

M. J. S.

Weil's Method for the Estimation of Sulphides. By F. Weil (*Bull. Soc. Chim.*, **47**, 680—682).—In reply to Friedheim's criticisms (this vol., p. 396) the author states that he does not employ an ammoniacal copper solution, but a solution containing 39·3375 grams of cupric sulphate, 197 grams of sodium potassium tartrate, and 125 grams of pure sodium hydroxide. The gases given off from the decomposition of the sulphide by hydrochloric acid are passed into an excess of this solution, the precipitated cupric sulphide filtered off, well washed, and the copper in the filtrate and washings titrated by means of a solution of stannous chloride. The results obtained by adhering to the details of the author's process are very concordant among themselves, and agree closely with results obtained by Fresenius' gravimetric method. A. P.

Detection of Nitrogen-compounds in Seleniferous Sulphuric Acid. By G. Lunge (*Ber.*, **20**, 2031—2033).—A solution of diphenylamine in sulphuric acid produces with seleniferous sulphuric acid, obtained by boiling selenium dioxide with pure sulphuric acid, a cornflower-blue colour indistinguishable from that formed when sulphuric acid containing nitrogen acids is similarly treated. The seleniferous acid, as is well known, yields a brownish-yellow or yellowish-red ring with ferrous sulphate or, preferably, ferrous chloride solution which, however, does not disappear on boiling, but darkens with the precipitation of red selenium, so that this test cannot be employed for the detection of nitrogen acids in sulphuric acid containing selenium-compounds, whilst in addition the indigo test cannot be relied on for this purpose, inasmuch as selenic acid oxidises indigo and cannot itself be reduced by boiling with hydrochloric acid without the simultaneous decomposition of the traces of nitrogen acids if these are present. Sulphuric acid containing selenium-compounds, however, gives no colour reaction with brucine, and this test is therefore available for the detection of nitrogen acids in seleniferous sulphuric acid W. P. W.

A Simple Nitrometer. By T. P. Blunt (*Pharm. J. Trans.* [3], **17**, 763).—A description of an improvised nitrometer for the rapid testing of "sweet spirits of nitre."

Colorimetric Estimation of Phosphorus. By F. Osmond (*Bull. Soc. Chim.*, **47**, 745—748).—When phosphomolybdic, arseniomolybdic, or silicomolybdic acids or their alkaline salts are dissolved in a solution of stannous chloride, a blue coloration is produced the intensity of which is proportional to the amount of the molybdic acid dissolved. This characteristic reaction may be employed to estimate the amount of phosphorus present in irons, steels, &c. The solution of stannous chloride is prepared by dissolving 12 grams of the crystallised salt in 80 c.c. of pure hydrochloric acid and making the solution up to a litre with distilled water. The precipitate of ammonium phosphomolybdate obtained in the usual manner is collected on an asbestos filter (filter-paper must not be employed as it absorbs the colouring matter) and then dissolved whilst on the filter by washing with a sufficient quantity of the stannous chloride solution. The filtered solution is then made up to 100 c.c. for each gram of the original substance taken by the addition of a further quantity of the stannous chloride solution, and the depth of the blue tint estimated by comparison either with standard solutions prepared from weighed quantities of ammonium phosphomolybdate (solutions thus prepared may be kept unaltered for several days), or with discs of tinted glass which have been carefully selected by comparison with the tints of solutions of known composition. The results obtained in this way agree very closely with those obtained by the usual method but are generally somewhat lower, a difference which varies between 0·002 and 0·010 per cent. A. P.

Apparatus for Determining Carbonic Anhydride in Carbonates. By D. Siderský (*Zeit. anal. Chem.*, **26**, 336—338).—This differs from Scheibler's well-known calcimeter mainly in having the graduated tube immersed in a cylinder of water instead of being connected with the usual pressure tube. M. J. S.

Portable Apparatus for the Estimation of Carbonic Anhydride in the Atmosphere. By O. Pettersson and A. Palmquist (*Ber.*, **20**, 2129—2134).—A portable modification of an apparatus devised for the estimation of aqueous vapour and carbonic anhydride in air at a constant temperature and pressure (this vol., p. 180). The sample of air directly drawn from the surrounding atmosphere, after saturation with aqueous vapour and measurement, is passed into an Orsat's potash tube, and allowed to remain for two minutes to complete the absorption of the carbonic anhydride present, then withdrawn and again measured. The correction required to compensate for the difference in humidity of the air analysed and that of the atmosphere from which it was taken is so small that it can be neglected. The estimation takes only a few minutes, and the results agree well with those obtained by other methods.

A modification of the method employed with the original apparatus (*loc. cit.*) is also described, which materially shortens the time required for the analysis. W. P. W.

Lithium Carbonate. By F. A. Flückiger (*Arch. Pharm.* [3], **25**, 509—515).—An aqueous solution of lithium carbonate saturated at 15° had the sp. gr. 1·0140, and contains 1 part of salt in 70·72 parts of water. A solution of freshly-ignited sodium carbonate in 50 parts of water had the sp. gr. 1·0208. Hence the presence of the latter salt in lithium carbonate can be readily detected by an excess of sp. gr. over 1·0137. In boiling water, lithium carbonate loses some of its carbonic anhydride; but a solution saturated at 15° may be heated on the water-bath for a day without losing any. The solubility of the salt diminishes as the temperature increases. A solution saturated at 15° and heated at 90° for some hours when quickly filtered and allowed to cool to 15°, had a sp. gr. of 1·009, and contained 1 part of the salt in 111·3 parts. By thus taking the sp. gr. of a solution prepared at 15° and one prepared at 90°, the presence of more soluble salts can be readily detected. A further characteristic property of lithium carbonate is its easy fusibility as compared with the corresponding sodium, potassium, and magnesium salts. J. T.

Titration of Zinc Powder. By F. Weil (*Bull. Soc. Chim.*, **47**, 877—879).—A reply to Kupferschlaeger. Zinc powder usually does not contain organic matter, but, even should it do so, neither that nor any carbon present would reduce the cupric chloride solution under the conditions specified for the working of the author's process. There is usually the merest trace of metallic cadmium in zinc powder; but whatever its amount, its reducing action is the same as that of zinc and would not affect the result. All metallic iron may be removed from zinc powder by means of the magnet. The valuation of zinc powder is based on the amount of metallic zinc, and any zinc oxide present is of no value. A. P.

Electrolysis of Copper and of Zinc. By A. Shand (*Pharm. J. Trans.* [3], **17**, 750).—Copper and zinc are more easily and accurately separated and estimated by electrolysis than by the ordinary processes. Certain essential details and precautions are described in the paper. R. R.

Estimation of Formic Acid and of Organic Matter in Water. By J. Klein (*Arch. Pharm.* [3], **25**, 522—531).—Formic acid in an alkaline solution is completely oxidised by an excess of potassium permanganate, as is well known, after boiling for a short time. After cooling to 70—80°, excess of standard oxalic acid is added, and then sulphuric acid. The excess of oxalic acid is now determined by a further addition of standard permanganate solution. If the sulphuric acid is added before the oxalic acid, oxygen is evolved and the results are inexact, as the author shows. The decomposing action of the sulphuric acid on the permanganate solution diminishes with the temperature. The foregoing is applied to the estimation of organic matter in water by the Schulze-Trommsdorff's method as follows:— 100 c.c. of water is boiled for ten minutes with 0·5 c.c. of aqueous soda solution (1 : 2) and 10 c.c. of centinormal permanganate solution. On cooling to 70—80°, 10 c.c. centinormal oxalic acid solution is added and 5 c.c. dilute sulphuric acid; the excess of oxalic acid is

titrated with permanganate solution, a blank experiment is made upon 100 c.c. of pure distilled water, and the difference is taken as due to organic matter in the water. J. T.

Determination of Hippuric Acid in Urine. By O. Völker (*Zeit. anal. Chem.*, **26**, 402).—Evaporate 200—300 c.c. of the urine to one-third in a thin glass basin; add 4 grams of sodium phosphate; concentrate to a syrup. Add excess of plaster of Paris, and dry till the mass can be powdered. Introduce the powder, together with the crushed basin into a Soxhlet's apparatus, and extract with freshly distilled light petroleum. After 4 to 6 hours, change the flask, extract for 6 to 10 hours with absolute ether and distil off the ether. Dissolve the residue in hot water; decolorise with charcoal; wash the charcoal well; concentrate at 50—60° to 1 or 2 c.c., and leave to crystallise. Rinse with the mother-liquor into a weighed filter; wash with a few drops of water and ether; dry and weigh. Add 0·0015 gram for every c.c. of filtrate. M. J. S.

Separation of Mineral Oils from Saponifiable Fats. By A. Gawalowski (*Zeit. anal. Chem.*, **26**, 330—331).—In separating mineral oils from those of animal and vegetable origin by saponifying the latter and extracting the former from the soap by light petroleum, it is necessary to use a considerable excess of alkali to ensure complete saponification; but this excess of alkali renders the soap to some extent soluble in light petroleum. This may be obviated by the following procedure:—The fat is saponified by alcoholic potash (2 parts of K_2O to 10 of fat); after evaporating off most of the alcohol, a solution of chloride of calcium, strontium, magnesium or sodium (? barium) is added, and then sodium hydrogen carbonate or sulphate till the alkalinity has nearly disappeared. The soap is then quite insoluble in light petroleum. M. J. S.

Test for Oil of Peppermint. By E. C. Federer (*Pharm. J. Trans.* [3], **17**, 808).—If 10 c.c. of pure oil of peppermint is shaken up with 20 c.c. of 94 per cent. alcohol, and 10 to 40 c.c. of cold water are then added, a clear supernatant oily stratum of 14 c.c. separates. With other oils and with admixtures separations occur different in their nature and volume, and of these an extended table is given in the paper. R. R.

Reaction of Strophanthin. By H. Helbing (*Pharm. J. Trans.*, [3], **17**, 924).—When a trace of strophanthin is dissolved in a drop of water, together with a trace of ferric chloride, the addition of a little strong sulphuric acid gives rise to a reddish-brown precipitate, which in an hour or two changes colour to a permanent emerald-green. R. R.

Urea Estimation. By C. Méhu (*J. Pharm.* [5], **15**, 607—609).—In estimating urea in albuminous urines by means of sodium hypobromite, it is frequently necessary to wait for hours before reading off the volume of nitrogen, on account of the persistent froth which results

from the reaction. This can be readily avoided by introducing a pilule of fat into the tube, and inclining the tube once or twice before placing it in position. J. T.

A Filter Tube for Use in the Estimation of Alkaloïds by Mayer's Reagent. By F. C. J. Bird (*Pharm. J. Trans.* [3], **17**, 826).—A small disc of thick filtering paper, interposed between two layers of muslin stretched over a small inverted funnel, arrests the passage of the precipitate produced by Mayer's reagent, the filtration being effected by suction, and the paper previously charged with French chalk, finely powdered, and suspended in water. R. R.

Theïne Estimation. By A. Lösch (*Arch. Pharm.* [3], **25**, 497—498).—10—20 grams of tea leaves are boiled twice with water, filtered, and washed with hot water until the wash-water runs colourless. The filtrate is mixed with calcined magnesia to the extent of one and a half times the weight of the leaves taken, and evaporated to dryness on the water-bath. The residue is finely powdered and extracted with hot chloroform. The chloroform extract is evaporated to dryness in a tared beaker, dried at 100—105°, and weighed. The theïne is thus obtained without loss and perfectly colourless. The method may be employed for the preparation of theïne on a large scale as the chloroform can be distilled off. J. T.

Coffee. By B. H. Paul and A. J. Cownley (*Pharm. J. Trans.* [3], **17**, 821 and 921).—When coffee is carefully roasted there is no appreciable loss of caffeïne. Infusion of coffee as made in France contains nearly the whole of the caffeïne present in the sample of coffee. Caffeïne can be easily and accurately determined both in roasted coffee and in mixtures of it, and its amount is the best means of determining the proportion of admixed substances. R. R.

Analysis of Coffees. By L. Padé (*Bull. Soc. Chim.*, **47**, 501—506).—The frequent cases which have occurred of coffees damaged by sea-water having been manipulated by washing and partial roasting has necessitated some certain but rapid means of detection; this the author finds may be attained by determining the specific gravity of the sample. The specific gravities of 24 varieties of genuine raw coffees varied between 1·368 and 1·041, whilst the specific gravities of the same samples after roasting varied between 0·635 and 0·500. Raw coffees therefore having a specific gravity below 1·000 may be suspected of being damaged samples washed and improved in colour by partial roasting.

A second method of sophisticating coffees consists in moistening the roasted berries with steam, in order to recoup the manufacturer for the loss of weight—17 to 19 per cent.—due to roasting, by this means berries may be made to absorb as much as 20 per cent. of water; the fraud may, however, also be detected by determining the specific gravity of the suspected sample, as it rises from about 0·635, the maximum of genuine roasted berries, to between 0·650 and 0·770.

The addition of artificial colouring matters such as the naphthol oranges may be readily detected by extracting the berries with alcohol in which such colouring matters are soluble, whilst genuine coffee does not yield a coloured solution.

The great inconvenience and difficulty of estimating the specific gravity of such a substance as coffee by the ordinary method with water, may be avoided by estimating the displacement of air due to a known weight of the berries by the following process. A weighed quantity of from 50 to 100 grams is placed in an air-tight cylinder the exact capacity of which is known, the air in the cylinder is then compressed by allowing mercury to rise to a given height in a tube attached, the usual corrections having then been made, the height of the mercury in a manometer gives the tension of the air in the cylinder, and the difference between this tension and the tension under similar conditions when the cylinder contains nothing but air indicates the volume of air, and hence the volume of solid matter contained in the cylinder. By this means very rapid and satisfactory determinations may be made. A drawing and full description of the apparatus employed by the author are given in the paper.

A. P.

Detection of Albumin in Urine. By L. Blum (*Chem. Centr.*, 1887, 345).—The usual test for the detection of albumin in urine, namely, the formation of a white coagulum on addition of meta-phosphoric acid, is inconvenient on account of the ready conversion of the meta- into pyro- or ortho-phosphoric acid. Instead of the free acid, the author prefers to use an acidified solution of a manganese salt to which has been added an excess of sodium metaphosphate. This can previously be tested by the addition of lead peroxide, which gives a rose-red coloration. The detection of the albumin is best effected by placing a few c.c. of the above solution in a test-glass and filtering the urine into it, when the albumin separates at the junction of the two liquids.

V. H. V.

Determination of Milk Constituents. By R. Palm (*Zeit. anal. Chem.*, **26**, 319—330).—By most of the existing methods of milk analysis, albumin and caseïn are the only proteïds determined, and the whole reducing power of the filtrate is ascribed to milk-sugar. Since, however, hemialbumose and the (perhaps identical) lacto-peptone of Millon and Commaille escape precipitation by the ordinary reagents and are capable of reducing Fehling's solution, the proportion of milk-sugar is over-estimated, and that of the total proteïds under-stated. Ritthausen's copper sulphate process suffers from this defect. Tannin, however, precipitates all the proteïds. The fresh precipitate digested at 30—35° with an excess of neutral lead acetate yields lead tannate and a solution of the proteïds in excess of lead acetate. After precipitating the lead by hydrogen sulphide, the amount of the proteïds is found by evaporating the filtrate and drying at 100°. Mercuric nitrate or acetate likewise precipitates all the proteïds, and by adding potash concurrently with the mercuric solution and finally in small excess, the solvent action of free acid or of an excess of mercuric salt

is prevented. A determination of the oxide of mercury (after drying at 100°) gives the proteïds by difference, or the fresh precipitate can be heated with baryta, the barium carefully precipitated by sulphuric acid and the proteïds weighed after evaporating the filtrate. A process which the author recommends for milk is as follows :—10 c.c. are evaporated to dryness; the residue is washed with light petroleum to remove fat, then with ether, which dissolves a small quantity of lactic acid formed during the evaporation, and therefore ought not to be employed for the fat determination. It is then well mixed with 0·2—0·3 gram of finely-ground ignited litharge and enough water to form a paste. This is again dried and then treated with water, when a clear filtrate is readily obtained containing the milk-sugar with some lead, whilst all the proteïds are left as an insoluble lead compound. The amount of each is ascertained by weighing after drying and then burning off the organic matter, using nitric acid to prevent reduction of lead. M. J. S.

General and Physical Chemistry.

Influence of Simple and of so-called Multiple Union of the Atoms on the Refractive Power of Compounds. Constitution of Benzene and Naphthalene Compounds. By J. W. Brühl (*Ber.*, **20**, 2288—2311).—Gladstone showed that the molecular refraction of aromatic compounds is always in excess of the value calculated from Landolt's formula. The author observed a similar excess in the case of all unsaturated compounds which are supposed to contain double union of atoms, the extent of the excess being dependent on the number of double combinations present. The atomic refraction of the saturated carbon-atom $rC' = 2{\cdot}48$, remains the same whether the four affinities are satisfied by single carbon-atoms or by monatomic substituents. Hence if benzene is represented by nine single carbon combinations it would possess a normal molecular refraction.

The molecular refractions of aldehyde and paraldehyde are 11·50 and 32·40 respectively; the latter number is three times the former less 2·10. This number is nearly the same as that obtained by multiplying the refraction-equivalent of the double combination of oxygen and carbon ($3 \times 0{\cdot}76 = 2{\cdot}28$).

Tables are given showing the molecular refraction of hydrocarbons C_5H_{10}, $C_{10}H_{20}$, and $C_{10}H_{16}$. The following conclusions are drawn:—That a so-called double combination of atoms is never optically equivalent to two single combinations, and that in the conversion of the former into the latter the increment of refraction disappears entirely or partially according as all or a portion of the multiple combinations are taken up. The author discusses the constitution of benzene, and considers Kekulé's formula to be established; carvacrol and carvol are probably constituted on the same model. Tables are given showing the refraction-equivalents of naphthalene and some of its derivatives; the numbers point to the presence of five ethylene combinations in naphthalene as shown in Erlenmeyer's formula. N. H. M.

Fluorescence of Spinel. By L. de Boisbaudran (*Compt. rend.*, **105**, 261—262).—Spinel usually gives a brilliant red fluorescence in a vacuum, but some specimens show a green fluorescence.

If a mixture of magnesia and alumina free from chromium is strongly heated, it yields spinel in fine granules which show no red fluorescence in a vacuum. A feeble green fluorescence is, however, visible, and its spectrum shows the green band observed with the green fluorescence of natural spinel. If the artificial spinel contains 0·1 per cent. of manganese oxide, it shows an intense green fluorescence, the spectrum of which consists of the same band. If 1 per cent. of chromic oxide is added the spinel shows a splendid red fluorescence. It follows that the green fluorescence of natural spinel is due to the presence of manganese, and the red fluorescence is due to the presence of chromium. C. H. B.

Crimson Line of Phosphorescent Alumina. By W. Crookes (*Proc. Roy. Soc.*, **42**, 25—31).—The author has repeated his previous experiments on this subject (*Phil. Trans.*, 1879, 660; *Ann. Chim. Phys.*, 1859, **57**, 50; *Proc. Roy. Soc.*, **32**, 206), and now gives careful measurements of the spectrum of phosphorescent alumina. This consists of a very faint pair of bands in the red, an intense crimson double line ($\lambda = 6942$ and 6937), a pair of faint and nebulous orange lines ($\lambda = 6707$ and 6598), and a continuous spectrum commencing at $\lambda = 6514$ and shading off into the green. The spectrum is different from that of spinel, first described by Becquerel, which shows a faint double band in the extreme red, a narrow crimson line ($\lambda = 6857$), four hazy red bands, and sometimes a continuous spectrum most intense in the green, and shading off gradually to blue and violet. A detailed description of this is given.

De Boisbaudran (this vol., p. 191) attributes the red fluorescence of calcined alumina, when submitted to the electric discharge in a vacuum, solely to the presence of chromic oxide. The author, however, has obtained the double line from pure alumina, quite free from chromium; and has found, moreover, that the line is reduced in intensity when a little chromium oxide is mixed with the alumina.

Alumina precipitated from its ammoniacal solution by boiling shows no crimson line, but simply a greenish phosphorescence; the red line is fully developed only when the earth is calcined at the highest temperature of the blowpipe flame. The author's previous experiments prove that physical differences may greatly influence the phosphorescence. In view of the possibility of the line belonging to some special variety of the earth, he has submitted pure alumina to three separate processes of fractionation, the operations being repeated 20 to 30 times in each case. Details are not given; but the result was that alumina giving the crimson line became concentrated towards one end of the fractionation, whilst the earth accumulating at the other end phosphoresced either green or hardly at all. Chromium was in no case detected.

It is thus still uncertain whether the line is due to alumina, but capable of being suppressed by the presence of some other earth; or if the line belongs to some accompanying earth; or if it depends on the mode of preparation of the alumina; or, lastly, if the molecule of ordinary alumina is complex and the line belongs to one of its constituents. Ch. B.

Fluorescences of Manganese and Bismuth. By L. de Boisbaudran (*Compt. rend.*, **105**, 45—48 and 206—208; see also this vol., pp. 3, 4, 89, and 873). The author has continued his researches, and has examined the fluorescences of a mixture of two solid solvents behaving towards one another as moderately active substances, and a third substance strongly fluorescent with one of the solvents only, as represented by a mixture of cadmium sulphate (100 parts), bismuth sulphate (10 parts), and calcium sulphate. With a proportion of calcium sulphate not exceeding 14·8 per cent., the calcium cadmium fluorescence is prevented by the presence of bismuth, although the calcium bismuth fluorescence is not visible. When the quantity of calcium

sulphate exceeds 16·1 per cent., the calcium bismuth fluorescence becomes visible, and increases in brilliancy with the proportion of calcium sulphate.

The author has also investigated the properties of a mixture of two solid solvents, the first of which (α) behaves towards the second (β) as a moderately active substance, and two active substances, one of which fluoresces with both solvents, and the other with only one of them. These conditions are fulfilled by a mixture of calcium, cadmium, bismuth and manganese sulphates. With an excess of calcium sulphate, the calcium manganese fluorescence is strongest, the calcium bismuth fluorescence much weaker, and the cadmium manganese fluorescence is not visible. With an excess of cadmium sulphate, the cadmium manganese fluorescence is predominant, the calcium manganese fluorescence is also visible, but the calcium bismuth fluorescence cannot be recognised.

The author's experiments lead to the following general conclusions. A substance may show strong fluorescence when disseminated through another substance, and yet show no fluorescence with a third substance closely analogous to the second. A substance may fluoresce strongly with one compound of a metal and not at all with another compound of the same metal; or it may show fluorescence of a different character in the second case. Strongly coloured substances prevent the fluorescence of active substances by reason of their strong absorptive power. A substance may behave as a solvent to one active substance; and also behave as a more or less active substance itself when mixed with a third substance. When two active substances coexist in the same solvent their individual fluorescences are reduced in intensity, but their spectral character is not altered. Two more or less active substances in the same solvent may, however, neutralise one another. A substance which is active under certain conditions, but is inert when mixed with a particular solvent, may yet reduce the effect of a substance which is usually active with this solvent. Fluorescence in a given solvent seems as a rule to diminish on the addition of a second solvent which is not so effective with the active substance as the first solvent, but in some cases this effect is very slight. An active substance generally produces a double fluorescence with a mixture of two active solvents, but with certain proportions one of the fluorescences diminishes in a greater ratio than the quantity of the solvent which produces it. With one active substance, and equivalent quantities of two effective solvents, the two fluorescences usually are equal in intensity, but the contrary is observed in certain cases. If two substances are unequally active with a given solvent, and the ratio of the two is kept constant whilst the proportion of the solvent is gradually increased, it is possible in some cases to observe successively (1) the effect of the less active body alone, (2) the coexistence of the two effects with increasing predominance of the effect of the more active substance. When the proportion of the more active substance is increased, its effect alone is observed whatever the nature of the solvent. Certain fluorescences which are masked by others can be seen when the tube is heated, or by observing immediately after the cessation of the electrical discharge, or by modifying the strength of the discharge.

C. H. B.

New Fluorescences with Well-defined Spectra. By L. de Boisbaudran (*Compt. rend.*, **105**, 258—261, 301—304, 343—348).—Mixtures of alumina with samarium oxide, $Z\alpha_2O_3$, or $Z\beta_2O_3$, treated with sulphuric acid and calcined, give fluorescences the spectra of which are characterised by a large number of well-defined lines and bands instead of by one or a few nebulous bands as is usually the case. Calcination at a very high temperature greatly increases the brilliancy of the fluorescences. The positions and characters of the bands and lines are described in detail.

Mixtures of alumina with uranium oxide give no fluorescence at all, and lanthanum and yttrium oxides give no well-marked fluorescences. Alumina and ytterbium oxide give a blue fluorescence, the spectrum of which consists of four bands, which are also observed in the fluorescences of mixtures rich in ytterbium and thulium, or erbium and thulium, and which therefore may be attributed to thulium or to a new element.

Mixtures of alumina with oxides of cerium, erbium, thulium, dysprosium, and gadolinium, have also been examined, and their fluorescences will be described in detail in a subsequent paper.

C. H. B.

Spectra of Didymium and Samarium. By E. Demarçay (*Compt. rend.*, **105**, 276—277).—The author has previously stated that the band at 4690 varies in intensity during the fractionation of praseodymium, and he concluded that the band was not due to praseodymium. The fact is confirmed but the conclusion is withdrawn. The purest fractions of praseodymium containing only small quantities of lanthanum show a strong nebulous band at about 4690, which, however, is very different in character from the band previously referred to, and it follows that there are two bands of very similar wave-length, but of different character, one being due to praseodymium and the other to some other element at present unknown.

Neodymium free from praseodymium and containing only a very little samarium, gave a spectrum in which the following bands not previously described were observed. A somewhat narrow band at about 4640 on the less refrangible side of a nebulous didymium band; a narrow and somewhat feeble band at 4300; and in a nitric acid solution a band at 4760, which really consists of two lines at 4734 and 4768 respectively, the more refrangible being the more intense. This double line is seen with pure neodymium.

The author anticipated Kruss, Nilson, and Gerhardt, in the discovery of the compound nature of samarium (Abstr., 1886, 837; and this vol., p. 551). C. H. B.

Development of Voltaic Electricity by Atmospheric Oxidation. By C. R. A. Wright and C. Thompson (*Proc. Roy. Soc.*, **42**, 212—216).—The authors have observed that when metallic copper immersed in aqueous ammonia is exposed to a limited supply of air, the metal dissolves chiefly as cuprous oxide. This action, which the authors regard as in all cases the primary action, is very slow when the liquid is kept perfectly at rest; but it can be greatly

accelerated by arranging horizontally near the surface of the liquid a plate, termed the "aëration" plate, of platinum or other conductor not acted on under the circumstances, and joining this to the copper by a wire. When connection is made through a galvanometer, it is found that a current is generated during the action. The voltaic element thus formed polarises rapidly unless the external resistance is very high. Its electromotive force varies from 0·5 to 0·6 volt, and increases with the concentration of the ammonia solution, or when sodium or ammonium chloride is added thereto, or when spongy platinum is substituted for the platinum plate. In the latter case, and with strong ammoniacal brine, it may amount to 0·8 volt, nearly equalling that due to the heat of formation of cuprous oxide (40810), or 0·88 volt.

This battery has a close connection with the air battery of Gladstone and Tribe (this Journal, 1873, 582), which consists of copper in solution of cupric nitrate, and an aëration plate formed by a trayful of crystals of silver nitrate. Cuprous oxide is here deposited on the aëration plate, whilst in the author's cell it is formed at the surface of the copper. This has been proved by means of a battery of special construction. After continued action, copper was found only in the liquid surrounding the copper plate.

The authors are continuing these experiments, and have found that metals not otherwise prone to oxidation (mercury, silver) may be similarly dissolved in appropriate liquids. Ch. B.

Alteration of Carbon Electrodes used for the Electrolysis of Acids. By H. Debray and Péchard (*Compt. rend.*, **105**, 27—30).—The battery used consisted of four Bunsen cells, and the electrodes had been purified by treatment with chlorine. When hydrochloric acid is electrolysed with carbon electrodes, the gas evolved at the positive pole is a mixture of chlorine, carbonic anhydride, and oxygen; in the case of sulphuric acid it is a mixture of oxygen and carbonic anhydride; and in the case of nitric acid a mixture of nitrogen oxides and carbonic anhydride. In all cases, the positive electrode undergoes disintegration, and the black powder which is formed, after being washed and dried in a vacuum, deflagrates at a temperature below a red heat, with evolution of carbonic anhydride and carbonic oxide. When nitric acid has been electrolysed, the gas also contains nitrogen.

The products were analysed by causing them to deflagrate in a vacuum, and collecting the water and oxides of carbon evolved. The deflagrated matter was then heated to bright redness in a porcelain tube, and the gas given off was collected and analysed.

The amount of water and oxygen contained in the product varies with the nature of the acid electrolysed and its degree of concentration. The proportion of oxygen is sometimes as high as 9 to 10 per cent., and that of water as high as 8 per cent.

In the case of hydrochloric acid, no soluble organic compound is formed. C. H. B.

Conductivity of Bismuth for Heat in a Magnetic Field. By A. Righi (*Compt. rend.*, **105**, 168—169).—The conductivity of bis-

muth for heat varies in a magnetic field in the same ratio as its electrical conductivity, and the isothermal lines undergo rotation in the same manner as the equipotential lines. C. H. B.

Comparative Radiation of Fused Platinum and Fused Silver. By J. Violle (*Compt. rend.*, **105**, 163—165).—The total radiation of melting platinum as measured by means of a smoked thermopile is 54 times as great as the total radiation of an equal surface of melting silver. This ratio is much less than that of the luminous intensities of the two metals. C. H. B.

Heat of Formation of Hydrogen Telluride. By Berthelot and Fabre (*Compt. rend.*, **105**, 92—95).—Tellurides of zinc, iron, and the alkalis do not yield pure hydrogen telluride. Better results are obtained with the tellurides of calcium, barium, and magnesium, especially the latter. Magnesium telluride is obtained by heating a mixture of the two elements to dull redness when combination takes place with great violence. A better method is to pass tellurium-vapour over magnesium heated in an atmosphere of pure hydrogen. The telluride is a white, flocculent substance, which alters very readily on exposure to air, and yields pure hydrogen telluride when treated with hydrochloric acid. The gas is very unstable even in the dark, and decomposes at once in contact with moist air. It is completely absorbed by potash. Its odour is different from that of hydrogen sulphide or selenide, and slightly resembles that of hydrogen arsenide, and its action on the animal economy is very much less irritating than that of the selenide. Its solution in alkalis is colourless, but becomes blue in presence of a trace of oxygen, tellurium being precipitated if the oxygen is in excess.

Hydrogen peroxide decomposes hydrogen telluride with formation of water and liberation of tellurium, but part of the latter undergoes oxidation. The reaction with ferric chloride is, however, very definite, and it was therefore used in the thermochemical measurements. The heat developed by the reaction ($TeH_2 = 130$) is 58·24 Cal., from which it follows that—

$$H_2 \text{ gas} + \text{Te cryst.} = TeH_2 \text{ gas absorbs } -35{\cdot}0 \text{ Cal.}$$

The heats of formation of water, hydrogen sulphide, and hydrogen selenide, are respectively + 59·0, + 4·6, and − 12·3 Cal., and it is evident that in the oxygen-group, as in the chlorine-group, the energy of combination with hydrogen diminishes as the atomic weight of the element rises. C. H. B.

Heat of Formation of Crystalline Tellurides. By C. Fabre (*Compt. rend.*, **105**, 277—280).—Tellurides can be prepared by passing the vapour of tellurium over the metal, or by heating the finely-divided metal with tellurium in an atmosphere of hydrogen. Ferrous telluride forms steel-grey crystals which scratch glass; cobalt telluride forms brownish crystals; nickel telluride forms small, reddish-grey crystals; thallium telluride resembles galena in appearance, but rapidly tarnishes in the air and is readily powdered. These tellurides

are not affected by cold hydrochloric and sulphuric acids, but slowly alter in moist air.

All the tellurides dissolve readily in bromine-water and bromine, with formation of hydrogen bromide, a metallic bromide and tellurous acid. This reaction was utilised for the determination of the heats of formation of the tellurides, and the numbers given in the following table are the heats of formation of the crystallised compounds from crystallised tellurium and the solid metal. The heats of formation of the selenides are given for comparison.

	Selenide.	Telluride.
Ferrous	18·44	15·58
Cobalt	18·88	15·30
Nickel	18·42	15·10
Zinc	40·40	37·22
Cadmium	24·20	19·96
Cuprous	20·84	14·30
Thallium	17·72	12·24
Lead	15·76	11·42

The heats of formation of the tellurides are lower than those of the corresponding selenides. C. H. B.

Values of the Heats of Combustion of Organic Compounds Determined by Different Methods. By F. Stohmann (*J. pr. Chem.* [2], **36**, 131—141).—A comparison of the results obtained by the author in his various researches with those published by Berthelot in conjunction with Vieille, Louguinine, and Recoura. A determination of the heat of combustion of naphthalene by Berthelot's method of combustion in compressed oxygen has given the value 1231·5 cal. W. P. W.

Passage from the Benzene Series to the Acetic Series. By Berthelot and Recoura (*Compt. rend.*, **105**, 141—145).—A further connecting link between the two series is furnished by the fact that quercite and inosite can both be converted into quinone.

Quercite.—Heat of combustion, 1 gram 4·330 Cal.; per gram-molecule at constant volume, +710·1 Cal.; at constant pressure, 709·8 Cal. Heat of formation (crystallised), +268·2 Cal.

Inosite.—Heat of combustion, 1 gram 3·703 Cal.; per gram-molecule at constant volume and pressure, +666·5 Cal. Heat of formation, +3·115 Cal. These values are slightly higher than those for glucose.

Quinic Acid.—Heat of combustion, 1 gram 4·342 Cal.; per gram-molecule, +833·7 Cal. Heat of formation (crystallised), +238·3 Cal.

The union of quercite with two atoms of oxygen to form inosite would develop +43·3 Cal., a number intermediate between the heat of conversion of benzene into phenol (36·6), and of phenol into quinol (+52·2). The formation of quinic acid and water by the union of quercite and formic acid would develop +53·9 Cal., a number comparable with the heat developed by the similar reaction between phenol and formic acid (+36·6). The conversion of inosite into quinone by removal of 4 mols. water would develop +9·7 Cal., and hence this is a case of dehydration with change of function, but with-

out condensation, accompanied by development of heat. The conversion of quercite into quinone by removal of 3 mols. H_2O would develop +24·9 Cal., and the conversion of quinic acid into hydroxybenzoic acid by a similar reaction would develop +98·7 Cal. The condensation of acetylene to benzene develops +171·0 Cal.

In all cases, the conversion by dehydration of compounds belonging to the acetic acid series into compounds of the benzene series is accompanied by a development of heat, or in other words by a loss of energy, which corresponds with the increased stability acquired by the nucleus of the fundamental hydrocarbon. C. H. B.

Boiling Points of Salt Solutions. By G. T. Gerlach (*Zeit. anal. Chem.*, **26**, 413—530).—The author has carefully redetermined the boiling points of solutions of about 40 salts, acids, and alkalis, making in each case a series of observations on solutions of different strengths. With the majority, the formation of a crust during ebullition begins a little below the highest temperature attainable. In the case of salts which crystallise with water of crystallisation, the salting out which occurs on further evaporation is accompanied by a fall of temperature, which in some cases is very considerable. The crystalline magma obtained by salting out sodium sulphate at the boiling point has been observed to boil at 72°, while the escaping steam showed 100°. If in a constant amount of water equal quantities of salt are successively dissolved, the differences in the boiling points invariably decrease, but if in the case of salts which crystallise with water of crystallisation, only the anhydrous salt is considered, the differences between the boiling points for equal increments of salt increase at first, and only begin to decrease when stronger solutions with higher boiling points are reached. This points to the existence, in the weak solutions, of compounds of salt and water acting as a single substance, even at the boiling temperature, and to the dissociation of these hydrated molecules at the higher boiling points.

By laying down the boiling points in curves, it is seen that when equal weights of the salts are regarded, the curves for different substances follow no regular law, and frequently cut one another. With equal equivalents (molecular weight divided by the valency of the metal) the curves of salts of the same group and similar constitution never cut.

No direct connection can be traced between the molecular weights of the dissolved substances and the boiling points of their solutions, nor between specific gravity or specific heat and boiling point. On the other hand, in most cases, solutions of highly soluble salts boil at higher temperatures (for equal molecular concentration) than those of lower solubility. Also those salts which in the act of dissolving produce the smallest amount of contraction are almost invariably those which for equal molecular concentration show the highest boiling points. Ammonium salts are the chief exceptions to both these laws.

Tammann's law that for a given temperature the lowering of the vapour-tension produced by dissolving one molecule of a salt in an invariable quantity of water is equal for salts of similar constitution, is not borne out by the author's observations. M. J. S.

Solidification of Liquids by Pressure. By E. H. Amagat (*Compt. rend.*, **105**, 165—167).—The author has examined a large number of organic and inorganic liquids at temperatures between 0° and 50°, and at pressures up to 3000 atmos., but has not observed any signs of solidification. Carbon tetrachloride, however, behaves differently, and solidifies at a high pressure, melting again when the pressure is released. The solid has a very distinct crystalline structure; solidification takes place under a pressure of 210 atmos. at −19·5°, 620 atmos. at 0°, 900 atmos. at 10°, and 1160 atmos. at 19·5°.

Carbon protochloride, C_2Cl_4, does not solidify under a pressure of 900 atmos. at 0°, but benzene seems to solidify at about 700 atmos. at 22°.

It is probable that every liquid possesses a critical point of solidification analogous to the critical point of gases, that is, a temperature above which no pressure, however great, will convert the liquid into a solid. C. H. B.

Dissociation of some Gases by the Electric Discharge. By J. J. Thomson (*Proc. Roy. Soc.*, **42**, 343—345).—When the vapour of iodine, at a temperature of 200—230°, is subjected in a tube exhausted of air to the action of the sparks from a coil giving a 3-inch spark in air, the pressure as indicated by a sulphuric acid manometer increases at first rapidly, then more slowly, and finally becomes stationary. On stopping the coil, the greater part of this increase is permanent, or at least lasts for some hours. The author attributes it to dissociation of the iodine-vapour. The amount of dissociation has been measured by observing the vapour-density in a special apparatus, sulphuric acid being excluded. The density after sparking then fell to 100, 115, 86, and 84 (H = 1) in different experiments. In the last case (temp. = 232°), after standing 24 hours, the dissociation still equalled that produced by Meyer at 1570°. The colour of the dissociated vapour is stated to be a little lighter and less uniform than that of the normal vapour. The electric strength was also reduced.

When bromine-vapour is sparked in a similar way, an increase of pressure also occurs, but disappears rapidly, probably owing to reunion of the separated atoms. Vapour-density determinations also showed that bromine is dissociated by simple heating at a low pressure for a long time. In such determinations, therefore, the vapour should be maintained at constant temperature for some time before observing.

Experiments have also been made with chlorine and nitrogen tetroxide. Ch. B.

Osmotic Equilibrium and the Concentration of Solutions by Gravitation. By Gouy and G. Chaperon (*Compt. rend.*, **105**, 117—119).—An application of the laws of thermodynamics to the question of osmotic equilibrium.

Demonstration of the Coefficient of Expansion of Gas as a Lecture Experiment. By R. Schiff (*Gazzetta*, **17**, 190—191).—In this paper, a simple apparatus is described for demonstrating the law

of the expansion of gases as a lecture experiment. In a graduated tube surrounded with a warming jacket is inclosed 273 c.c. of dry gas; the tube is connected with a piece of flexible tubing, bent in the form of a U, and provided with a mercury reservoir. Previous to the experiment the level of the mercury in both limbs is adjusted, the tube heated with steam, and the level readjusted. If the barometric pressure has remained the same, the reading on the tube will give the coefficient of expansion. V. H. V.

Estimation of Pressure in Closed Tubes. By A. Reychler (*Ber.*, **20**, 2461—2462).—In this paper, a simple apparatus is described by means of which the pressure in sealed tubes may be roughly estimated. It consists of a glass tube of small diameter, about 40 cm. long, one end of which is sealed off, and 4—5 cm. length from this end is silvered; the tube is then bent in the form of a U, and filled to a certain height with mercury. The whole is enclosed in the tube in which it is proposed to carry on the reaction at an increased pressure, which forces down the mercury in the open limb, thus causing it to rise in the sealed limb and dissolve off the silver. Then from the rise of level of mercury thus determined and the tension of the vapour of mercury at the temperature of the reaction, the pressure within the tube can be directly calculated. V. H. V.

Inorganic Chemistry.

Selenium Alums. By C. Fabre (*Compt. rend.*, **105**, 114—115).—The author has prepared the selenium alums of the following bases:—Sodium, potassium, cæsium, rubidium, thallium, ammonium, ethylamine, diethylamine, triethylamine, methylamine, dimethylamine, trimethylamine, and propylamine, by mixing solutions of the corresponding selenate and aluminium selenate. The products have the general composition and crystalline form of the alums, and are colourless. The cæsium and rubidium selenium alums are much more soluble than the corresponding sulphur-alums, and it is worthy of note that the soluble thallium alum is formed from a selenate which is almost insoluble in water. The organic alums closely resemble the ammonium salt.

By mixing violet chromium selenate with the selenates of potassium, sodium, cæsium, rubidium, thallium, ammonium, ethylamine, and propylamine, the corresponding alums were obtained. They crystallise well, and frequently form very distinct octahedra. They are violet-red by transmitted light, and their solutions are violet when cold, but become green at 55—60°. The green solutions will only crystallise when allowed to evaporate spontaneously for several months. Thallium chromium selenium alum is deep violet by transmitted, and almost black by reflected light. C. H. B.

Monoclinic Form and Optical Properties of Prismatic Arsenious Anhydride. By Des Cloizeau (*Compt. rend.*, **105**, 96—99).—Prismatic arsenious oxide belongs to the monoclinic system. Measurements of the various angles are given. The angle of the prism is 135° 1′, and is similar to that of valentinite or prismatic antimonious oxide, 137° 7′, but as the other zones of the crystals are not similar the two compounds are not strictly isomorphous. The crystals are highly birefractive, the plane of the optical axis being parallel with the plane of symmetry.

The fact that thin plates of ordinary arsenious oxide are sometimes feebly birefractive, indicates that the crystals are possibly only pseudo-cubic. C. H. B.

Preparation and Properties of Carbon Oxysulphide. By P. Klason (*J. pr. Chem.* [2], **36**, 64—74).—To prepare this substance, Than recommends (*Annalen*, Supp. **5**, 245) the addition of solid potassium thiocyanate to a cold mixture of 5 vols. strong sulphuric acid and 4 vols. water. The author finds that the purest product and best yield is obtained on adding 50 c.c. of a concentrated aqueous solution of potassium or ammonium thiocyanate to a cooled mixture of 290 c.c. (520 grams) of strong sulphuric acid and 400 c.c. water. The whole is heated at 25° in a water-bath. The gas thus prepared contains only about 2½ per cent. of carbonic anhydride and 0·05 per cent. of carbon bisulphide. Hofmann recommends passing the gas through an ethereal solution of triethylphosphine to free it from carbon bisulphide. The author finds that the absorption of this latter is much more rapid and complete if a small quantity of pure triethylphosphine is used instead of a solution, the gas being then passed through pure sulphuric acid to free it from traces of the phosphine. Carbon oxysulphide is only absorbed very slowly by a 33 per cent. aqueous solution of potash. If the gas obtained as above is passed slowly through about 20 cm. of such a solution, the whole of the carbonic anhydride is absorbed with a loss of only about 7 per cent. of the oxysulphide. A 33 per cent. aqueous solution of potash mixed with its own volume of alcohol absorbs carbon oxychloride completely and rapidly, and is the best reagent for use in estimating it.

Pure carbon oxysulphide is odourless and tasteless. Its physiological effects are very similar to those of nitrous oxide. When passed through a saturated solution of baryta, no opalescence is produced for at least half a minute, whilst if any carbonic anhydride is present, the solution becomes milky at once. With lead acetate solution, the precipitate is a quarter of an hour forming. L. T. T.

Action of Chlorine on Carbon Bisulphide and of Sulphur on Carbon Tetrachloride. By P. Klason (*Ber.*, **20**, 2376—2383).—Carbon bisulphide is but slightly attacked by chlorine at ordinary temperatures, but in presence of chlorine-carriers, especially of iodine, action takes place readily with the ultimate formation of carbon tetrachloride. The author has carefully studied this reaction and the intermediate products formed, and also the derivatives

obtained by the action of heat, reducing agents, &c., on such compounds. He has isolated the following compounds:—Thiophosgene, $CSCl_2$, boiling at 73·5°, and gradually changing to its polymeride; trichloromethylsulphur chloride, $CCl_3{\cdot}SCl$, boiling at 149°; *trichloromethyl bisulphide*, $CCl_3{\cdot}S_2{\cdot}CCl_3$, boiling at 135° in a vacuum; trichloromethyl trisulphide, $CCl_3{\cdot}S_3{\cdot}CCl_3$, crystalline, and boiling at 190° in a vacuum; and *chlorothio-carbonylsulphur chloride*, $CSCl{\cdot}SCl$, boiling at 140°. The compound $CCl_3{\cdot}S_3{\cdot}CCl_3$ is identical with that described by Rathke as $S(CCl_2{\cdot}SCl)_2$.

In the action of sulphur on carbon tetrachloride, only carbon bisulphide, sulphur chloride, and sometimes traces of thiophosgene and $CCl_3{\cdot}SCl$ were formed. L. T. T.

Manganese Compounds. By B. Franke (*J. pr. Chem.* [2], **36**, 166—174).—The blue gas formed when air or carbonic anhydride saturated with aqueous vapour at 40—50° is led over the manganese oxysulphate $(MnO_3)_2SO_4$ (this vol., p. 893), is free from ozone, and consists of a new gaseous oxide of manganese, probably *manganese tetroxide*, MnO_4, which condenses to a blue-violet amorphous substance at a lower temperature. The quantity obtained was too small to allow of analysis; the compound itself differs, however, in its properties from the trioxide and heptoxide; it is more volatile than the trioxide, and is less readily acted on by water, with which it combines to form manganic acid with the liberation of oxygen. The tetroxide is decomposed by the action of sulphuric acid and ether.

When warm and moderately strong sulphuric acid is treated with potassium permanganate until the brown solution no longer dissolves the salt, and the mixture is heated, a beautifully crystalline, claret-red salt, $2Mn_5(SO_4)_8 + 5K_2SO_4$, is obtained. This salt dissolves in dilute sulphuric acid with a brown colour, and in concentrated sulphuric acid with a blue-violet colour, decomposes on heating into potassium and manganese sulphates, oxygen and sulphuric anhydride, and when treated with much water yields the hydroxide $3MnO_2,2H_2O$, and manganese sulphate. Small, yellowish, lustrous scales of a *manganic manganous oxide*, Mn_5O_8, are obtained, however, if the salt is added to water, the mother-liquor removed as quickly as possible, and the residue washed with water, alcohol, and finally with ether. On treatment with dilute sulphuric acid, the oxide yields manganese sulphate (2 mols.), and the hydroxide $3MnO_2,2H_2O$ (1 mol.); it may therefore be regarded as $3MnO_2,2MnO$. When heated, it is converted into trimanganic tetroxide, Mn_3O_4. W. P. W.

Thorium Silicates. By L. Troost and L. Ouvrard (*Compt. rend.*, **105**, 255—258).—When thorium oxide is fused with silica and calcium chloride at a bright red heat, and the crystalline product is treated with water, and then with hydrochloric acid to remove calcium chloride and silicate, a residue of small, rhombic crystals is left, which are insoluble in acids, but are attacked by potassium hydrogen sulphate; sp. gr. at 16° = 6·82. They have the composition $2ThO,SiO_2$ or ThO_2,SiO_2, but are not isomorphous with zircon. The thorium may, however, be present in the form of a dioxide, and this supposition

is supported by Krüss and Nilson's recent determination of the vapour-density of thorium chloride. These numbers were always lower than those required by the formula $ThCl_4$, but the authors have repeated the determination by Dumas' method, and have obtained similar though somewhat higher numbers. In this case, the influence of the hydrogen chloride formed by the action of a small quantity of absorbed moisture on the thorium chloride would be less marked, because the greater part of the gas is expelled together with the nitrogen with which the globe is filled. In Victor Meyer's method, on the other hand, a small quantity of substance is taken, and the hydrogen chloride evolved may introduce very considerable errors.

If the thorium oxide, silica, and calcium chloride are fused together at 1100°, and the product treated with water and hydrochloric acid, a residue of crystals and granules is obtained. The latter are attacked by potassium hydrogen sulphate, whilst the former are not affected, and thus they can be separated. The crystals are triclinic, with an angle of extinction of about 31°; sp. gr. at 25° = 5·56. They have the composition ThO,SiO_2 or $ThiO_2,2SiO_2$. This silicate is therefore not analogous to zircon in form or composition, just as thorium metaphosphate is not analogous to silicon metaphosphate (Abstr., 1885, 1113).

C. H. B.

Thorium Sodium and Zirconium Sodium Phosphates. By L. Troost and L. Ouvrard (*Compt. rend.*, **105**, 30—34).—Sodium metaphosphate fused at a red heat readily dissolves thorium oxide, amorphous thorium phosphate, and anhydrous thorium chloride, and the product is completely soluble in water after cooling. If, however, the thorium compound is added to saturation, and the fused mixture is allowed to cool slowly and extracted with water, a residue is left, consisting of elongated, triclinic prisms, which act strongly on polarised light, the angle of extinction being about 44° whilst the angle of the axis is 45° and the twinning plane is parallel with the plane of the optical axes. The crystals are insoluble in hydrochloric or nitric acid and in aqua regia, and have the composition $Na_2O,8ThO,3P_2O_5$ (Th = 116·2), or $Na_2O,4ThO_2,3P_2O_5$ (Th = 232·4). They are therefore analogous to the compound previously obtained with potassium metaphosphate (Abstr., 1886, 853).

Zirconium oxide, phosphate, and chloride are less readily soluble in sodium metaphosphate, and the product is a crystalline powder composed of feebly birefractive rhombohedra, extinction taking place along the diagonals. It is insoluble in acids and in aqua regia, and has the composition $Na_2O,4ZrO_2,3P_2O_5$; sp. gr. at 12° = 3·10.

When fused sodium pyrophosphate is mixed with thorium oxide or phosphate, it yields an insoluble powder, consisting of very thin hexagonal, microscopic leaflets. If sodium chloride is added to the mixture, solidification takes place more slowly, and the product is obtained in hexagonal lamellæ, mixed with fragments of hexagonal prisms which act on polarised light, and are soluble in nitric acid. They have the composition $5Na_2O,4ThO,3P_2O_5$ or $5Na_2O,2ThO_2,3P_2O_5$. If the fused substance is mixed with excess of sodium chloride, thorium oxide is precipitated in minute cubes.

Thorium chloride and sodium pyrophosphate yield birefractive

crystals, which probably belong to the triclinic system. They have the composition Na_2O,ThO_2,P_2O_5. Zirconium oxide or phosphate added to the fused pyrophosphate, yields a crystalline powder. Zirconium chloride added to the pyrophosphate together with a small quantity of sodium chloride, yields hexagonal plates, which act very feebly on polarised light, and are soluble in acids. Sp. gr. at 14° = 2·88. They have the composition $6Na_2O,3ZrO_2,4P_2O_5$. With a larger quantity of sodium chloride, the compound $4Na_2O,ZrO_2,2P_2O_5$, is obtained in prisms which act strongly on polarised light, and have a negative bisectrix. They are soluble in acids. Sp. gr. at 14° = 2·43.

On account of its comparative infusibility, normal sodium phosphate alone yields no similar products, but when mixed with sodium chloride it yields the same products as the pyrophosphate.

Thorium sodium and zirconium sodium metaphosphates are similar to one another and to the corresponding potassium compounds (*loc. cit.*), but they are not isomorphous. The double pyrophosphates are not analogous to one another either in form or composition. These results afford no evidence as to the true atomic weight of thorium and the formula of its oxide. C. H. B.

Vanadates. By A. Carnot (*Compt. rend.*, **105**, 119—122).—When ammonia is added gradually to a cold acid solution containing vanadic acid, the yellow colour becomes deeper and deeper, up to the point at which the reaction becomes neutral; the colour persists for a long time if the liquid remains cold. Conversely, if an acid is added gradually to a colourless alkaline solution of a vanadate, the yellow colour appears as soon as the reaction becomes acid, but diminishes in intensity when excess of acid is added. These facts indicate that in almost neutral solutions acid vanadates are formed with a deeper colour than that of vanadic acid itself. The reactions of such solutions with metallic salts are different from those observed under ordinary conditions, various acid vanadates being formed. In order to ensure the formation of normal vanadates, an ammoniacal solution should be only partially neutralised, or the liquid should be boiled in presence of a slight excess of ammonia.

Cobalt and Nickel.—Cobalt nitrate and vanadic acid in a solution exactly neutralised with ammonia give an orange precipitate of the vanadate CoO,V_2O_5. Precipitation is complete after several hours if the liquid is neutral, but takes place more slowly in presence of any ammonium salt other than the nitrate. Nickel yields a similar precipitate, but its formation takes place more slowly, and is prevented by the presence of ammonium nitrate. Hot solutions of nickel and cobalt salts yield respectively pale-yellow and brown precipitates, but precipitation is always incomplete, and is prevented by ammonium chloride.

Zinc salts with neutral vanadates give yellow precipitates, which become white when heated. Zinc nitrate and ammonium vanadate yield a white precipitate, easily soluble in acids and in ammonia, the whole of the vanadic acid being precipitated.

Cadmium salts in neutral solutions yield a white precipitate, readily

soluble in the slightest excess of acid or ammonia. Precipitation is always incomplete.

Copper salts in the cold give a greenish-yellow precipitate of the vanadate CuO,V_2O_5, which becomes greenish-brown when heated. If the solution is hot, the precipitate is brownish-yellow, and becomes black when boiled. It has the composition $2CuO,V_2O_5$. In both cases precipitation is incomplete, and if ammonium sulphide is added a black precipitate is formed, and the liquid is brown; the precipitated sulphide contains vanadium, and the liquid contains copper. On acidifying the liquid, a rose-brown copper vanadium sulphide is precipitated. Arsenates and copper salts behave in a similar manner.

Mercurous nitrate in neutral solutions precipitates the whole of the vanadic acid in the form of the orange vanadate, Hg_2O,V_2O_5. In presence of a slight excess of ammonia, a grey or blackish precipitate of complex composition is formed. When these precipitates are heated in hydrogen sulphide, vanadium sulphide is left in a pure condition, and this method may be used for the isolation and estimation of vanadium. Mercuric chloride produces no precipitate if the solution is acid, but on adding ammonia, a pale-yellow precipitate is formed. If the liquid is neutral when the mercuric chloride is added, the precipitate is white. Precipitation is complete, and this method may also be used for the isolation of vanadium in the manner just described.

Lead salts yield a precipitate which is pale yellow in presence of a slight excess of acetic acid, yellowish in presence of a slight excess of ammonia. Precipitation is almost complete in neutral solutions.

Bismuth nitrate precipitates the whole of the vanadic acid as a yellowish-white precipitate on addition of ammonia. If the liquid is slightly acid, an orange precipitate is formed on boiling, but precipitation is incomplete. If the acid liquid is mixed with sodium acetate and then boiled, a bright yellow precipitate of the vanadate Bi_2O_3,V_2O_5 is formed. This becomes orange when heated, but regains its yellow colour on cooling. C. H. B.

Atomic Weight of Gold. By G. Krüss (*Ber.*, **20**, 2365—2368).—Referring to the discrepancy between his own (this vol., p. 778) and Thorpe and Laurie's (Trans., 1887, 565) determinations of the atomic weight of gold, the author points out that in one of his papers on gold (*Annalen*, **238**, 265), he has shown that potassium aurobromide always contains about 0·05 per cent. of free gold, probably formed during crystallisation by the reducing action of organic matter in the air. Thorpe and Laurie have not taken account of this fact. Applying this correction to Thorpe and Laurie's determination, the atomic weight obtained by means (1) of the ratio Au : KBr becomes 196·616; (2) of the ratio Au : Ag, 196·559; (3) of Au : AgBr, 196·575, or lower than the number 196·64 previously obtained by the author. The author therefore upholds the correctness of his determinations. L. T. T.

Gold Sulphides. By L. Hoffmann and G. Krüss (*Ber.*, **20**, 2369—2376).—The statements given in various text-books concerning the sulphides of gold are very conflicting, compounds Au_2S,

Au_2S_2, and Au_2S_3 being variously given. The sulphide Au_2S_2 is perhaps usually accepted, the existence of the other two very often disputed. These conclusions are, however, by no means justified. Berzelius believed he obtained Au_2S by passing hydrogen sulphide into a boiling solution of auric chloride. Levol, on the other hand, states that under these conditions free gold is alone deposited. The author finds that Levol's statement is correct, if care is taken to keep the temperature of the whole solution at 100°. If local cooling takes place the precipitate contains varying proportions of combined sulphur, but no definite compound can be obtained. In all their experiments the authors washed the precipitated sulphide by decantation with water, alcohol, ether, and carbon bisulphide successively. They found that the free sulphur was retained very firmly, and could not be completely removed by washing on the filter.

When hydrogen sulphide was passed through a solution of potassium aurocyanide, no apparent change took place, but when excess of hydrochloric acid was added, and the whole heated, *aurous sulphide*, Au_2S, was precipitated as a steel-grey precipitate. This was carefully washed as above, and obtained in a dry state as a brownish-black powder of constant composition, corresponding with the above formula. When freshly precipitated, it dissolves in water to a brown solution. It is therefore necessary in purification to wash it with water containing hydrochloric acid, in which it is not soluble. When once dried, it is no longer soluble in water. It is not decomposed when boiled with dilute hydrochloric or sulphuric acids. Aqua regia, chlorous oxide, and other oxidising agents oxidise it easily. Bromine-water slowly dissolves it, with formation of $AuBr_3$ and sulphuric acid. Alkaline monosulphides dissolve it but slowly and slightly, polysulphides rapidly and completely, with the formation of green solutions of sulpho-salts. Caustic potash solution does not attack it even at 100°, whereas the compound Au_2S_2 is, under like conditions, decomposed into gold, potassium gold sulphide, and potassium gold oxide. Potassium cyanide dissolves it readily, and the sulphide is reprecipitated by boiling the solution with excess of hydrochloric acid. This reaction gives a good means of purifying the sulphide from free sulphur, as a slightly warmed solution of potassium cyanide dissolves the former and not the latter. When heated in a tube, part of the sulphur distils off, and part passes off as sulphurous anhydride. The compound is completely decomposed at 240°, and ignites in oxygen at a low temperature. When heated in a stream of hydrogen, hydrogen sulphide is formed, but in a stream of hydrogen chloride the sulphur sublimes without the formation of any hydrogen sulphide, and pure gold is left.

The existence of a soluble aurous sulphide and a soluble aurous oxide (Krüss, *Untersuchungen über das Atomgewicht des Goldes*, München, 1885) speaks strongly in favour of placing gold in the alkali-group rather than in the platinum-group. L. T. T.

Mineralogical Chemistry.

Trona, Idrialine, and Zinc-bloom. By V. v. Zepharovitch (*Zeit. Kryst. Min.*, **13**, 135—144).—1. *Crystals of Trona*, $Na_6C_4O_{11} + 5H_2O$. — The author has measured 50 crystals of trona from the soda works of Ebensee. The axial ratio he found to be $a : b : c = 2{\cdot}8459 : 1 : 2{\cdot}9696$. $\beta = 77° 23'$. Analysis gave the following results :—

CO_2.	Na_2O.	H_2O.	Na_2SO_4.	Total.	Sp. gr.
38·93	40·77	19·96	0·20	99·86	2·14

2. *Idrialine Crystals from Idria.*—The discovery of idrialite in pistachio-green nodules in the Idria mercury mines was announced by R. Scharitzer (Abstr., 1883, 427). In 1886, specimens of a new variety were found. The specimens are of a yellowish-green to sulphur-yellow colour, and consist of pure idrialine. Microscopic examination shows that the plates belong to the monoclinic system.

3. *Fibrous Zinc-bloom* (*Hydrozincite*) *from Carinthia.* — It has hitherto not been observed that hydrozincite frequently exhibits a finely fibrous texture, especially in the reniform masses produced from the alteration of smithsonite. Analysis of some remarkably fibrous specimens of hydrozincite on galena recently obtained at Bleiberg, gave the following results (I) :—

	CO_2.	ZnO.	PbO.	H_2O.	Fe_2O_3.	SiO_2.	Total.
I.	17·05	70·76	1·26	10·30	0·42	0·36	100·15
II.	17·05	69·79	1·26	10·12	—	—	—

After subtracting the percentages of silica present as hemimorphite, and of iron present as limonite, the remainder (II) corresponds with the formula $4ZnCO_3 + 5Zn(HO)_2 + H_2O$. This formula does not agree with any yet given. B. H. B.

Turquoise from the Kirghise Steppes. By N. J. v. Kokscharoff (*Zeit. Kryst. Min.*, **13**, 187).—A greenish-blue mineral from the Karkaralinsk district of the Province of Semipalátinsk gave on analysis the following results :—

P_2O_5.	Al_2O_3.	Fe_2O_3.	Cu_2O.	Loss on ignition.	Total.	Sp. gr.
34·42	(35·79)	3·52	7·67	18·60	100·00	2·887

These results show that the new turquoise is characterised by an exceptionally high percentage of copper. It is not soluble in hydrochloric acid or nitric acid, although it is in alkalis. B. H. B.

Epsomite from Poland. By W. K. Zglenitzkij (*Zeit. Kryst. Min.*, **13**, 200—201).—In an abandoned level in the Tscharkoffy Sulphur Mines, the author observed an efflorescence having a saline bitter taste. Analysis showed that the mineral had the composition $MgSO_4,7H_2O$. Hitherto, epsomite has not been found in Russia any-

where except in the Siberian Steppes. At Tscharkoffy, it occurs in an argillaceous marl, of Upper Cretaceous age, in which well-preserved remains of *Ananchytes ovata* are found. The marl contains magnesia, and encloses beds of gypsum and sulphur. The hydrogen sulphide, formed from the decomposition of gypsum in the presence of organic remains, may be detected throughout the mine, and, on decomposition, yields sulphur and sulphuric acid or epsomite. B. H. B.

Augite from the Whin Sill. By J. J. H. Teall (*Zeit. Kryst. Min.*, **13**, 180—181).—The author gives the following two analyses of augite: I, from the normal Whin Sill (diabase containing bronzite), from Cauldron Snout; sp. gr. about 3·3; II, from the coarsest variety of the Whin Sill rocks, half a mile south of Tyne Head; sp. gr. 3·33.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	49·03	5·46	—	15·57	0·22	15·34	11·66
II.	48·41	4·05	2·36	15·08	0·37	15·98	12·14

	Na_2O.	H_2O.	Total.
I.	1·24	0·81	99·33
II.	—	1·19	99·58

The analysis of the first augite corresponds with the formula $14CaFeSi_2O_6 + 5CaMgSi_2O_6 + 6Mg_2Si_2O_6 + 3MgAl_2SiO_6 + MgFe_2SiO_6$. B. H. B.

Andesine from Scourie Bay, Sutherlandshire. By J. J. H. Teall (*Zeit. Kryst. Min.*, **13**, 181).—A vein of nearly pure felspar occurs in a dyke of hornblende schist at Scourie Bay. The principal cleavage of the felspar is parallel to the brachypinacoid. The sp. gr. is about 2·644. Analysis gave the following results:—

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Total.
58·16	26·66	5·79	0·65	6·99	1·76	100·01

B. H. B.

Minerals from Porthalla Cove, Cornwall. By J. H. Collins (*Zeit. Kryst. Min.*, **13**, 180).—The author gives the following analyses of minerals from the rocks of Porthalla Cove:—

	I*a*.	I*b*.	I*c*.	I*d*.	II	III.
SiO_2	38·60	37·15	39·50	43·35	44·01	43·16
Al_2O_3	0·10	5·60	5·08	4·08	11·95	28·50
Fe_2O_3	11·55	1·10	8·12	10·74	8·58	4·50
FeO		8·80			2·84	
CaO	trace	0·10	trace	1·51	10·51	17·08
MgO	33·62	32·80	34·65	28·43	16·15	2·84
Alkalis	3·31	0·29	0·10	1·35	2·25	1·50
H_2O at 100°	12·82	0·46	0·55	1·85	0·51	0·10
H_2O on ignition		13·70	12·00	8·69	3·20	1·50
Totals	100·00	100·00	100·00	100·00	100·00	99·18

I. Serpentine from Porthalla Cove, mostly associated with hornblende schist; *a*. greyish-green and granular, sp. gr. 2·65; *b*. dark green, sp. gr. 2·56; *c*. reddish-brown and granular, sp. gr. 2·545; *d*. dark red, sp. gr. 2·644. II. Hornblende from the Porthalla hornblende-schist. III. Plagioclase (anorthite) from the same rock, slightly weathered. B. H. B.

Microscopic Crystals of Albite in Calcareous Rocks of the Western Alps. By C. Lory (*Compt. rend.*, **105**, 99—101).—The author has shown many years ago that the dolomites and limestones of the triassic formation of the Western Alps contain microscopic crystals of albite, often accompanied by bipyramidal quartz and lamellæ of mica. The albite crystals are better developed the more crystalline the limestone in which they occur, but the occurrence of the crystals is not necessarily connected with the general crystalline character of the triassic beds.

The limestones of the lias are not crystalline with the exception of the liassic marble at Villete, which contains crystals of albite, but this is an exceptional deposit and rests directly on the trias. Albite crystals are also found in a very compact, white, nummulitic limestone in the bed of Montricher, near St. Jean de Maurienne.

The genesis of these albite crystals, which has taken place chiefly in the triassic limestones of the Western Alps, has also occurred exceptionally in middle lias and eocene beds. The formation of the crystals is connected with the special nature of the deposits in which they are found and the conditions which have favoured the crystallisation of the latter. C. H. B.

Composition of Volcanic Rocks. By L. Ricciardi (*Gazzetta*, **17**, 141—154).—The results of analyses of the volcanic rocks of Italy show that their composition is modified by successive eruptions. Thus the eruptive matter emitted from submarine volcanoes in past times was of an acidic nature, and contained about 73 per cent. of silica, but this has gradually changed to a basic character, and now contains only about 48 per cent. of silica. Several examples of this gradual modification are adduced. On the other hand, Etna and Vesuvius, which are always more or less active, have emitted within the last three centuries a product of constant composition, of the basic type. In order to explain this conversion from the acidic or trachytic form into the basic, which is especially exemplified in the case of the submarine volcanoes of Euganei and Pantelleria, the author suggests that the change is brought about by a reaction between the solid constituents of the Mediterranean Sea and the primordial rock. Thus, within the volcanoes, the chlorine is converted into hydrogen chloride by the dissociation of the water, and the radicles SO_4 and CO_3 are emitted as sulphurous and carbonic anhydrides, whilst the remaining constituents react with and modify the original rock. In this paper, it is shown that if a typical substance compounded of the fixed residue of the Mediterranean is compared with an argilliferous pliocenic marl, then this substance, mixed in proportions successively decreasing from 50 to 1 with one

proportion of an original trachytic rock as pantellerite, would give products of percentage composition similar to those of the various typical rocks from more recent to more ancient times. For the present, these considerations are limited to the volcanic rocks of Italy, as better studied than other examples, although geological evidence tends to show that similar phenomena occurred in the granitic plateau of central France and in Hungary. Further analyses of the matter emitted in recent eruptions of volcanoes situated in various parts of the world show that the first substance elaborated is always granite. V. H. V.

Meteorite at Djati Pengilon, Java. By Daubrée (*Compt. rend.*, **105**, 203—207).—This meteorite fell on March 19th, 1884, and weighed 166 kilos. It possesses a high tenacity, and does not readily break under the hammer. The fractured surface shows a remarkably large number of small cleavage faces, and resembles certain fine-grained felspathic rocks; the crust is not firmly adherent. Mean sp. gr. of the meteorite 3·747.

According to an analysis by Retgers, it consists of nickeliferous iron, 21·3; triolite, 5·1; olivine, 33·4; bronzite, 39·0; and chromite, 0·1 per cent. The metallic portion consists of iron, 88·68; nickel, 10·78; and cobalt, 0·54 per cent. Thin slices of the meteorite are transparent, but contain opaque and tuberculous granules. The olivine and bronzite both contain inclosures.

This meteorite belongs to a somewhat rare type, and is identical in lithological character with one which fell at Tjabé, a neighbouring place, on September 19th, 1869. C. H. B.

Organic Chemistry.

Solid α-Dichlorethyl Cyanide and its Conversion into Triethyl Cyanuride. By R. Otto and K. Voigt (*J. pr. Chem.* [2], **36**, 78—98).—This compound melting at 73—74° was first obtained together with its liquid isomeride by Otto. It crystallises in the clinorhombic system. The lower the temperature at which the chlorination of the propionitrile is carried out, the larger the quantity formed. It would seem to be a polymeride of the liquid compound, the polymerisation being in all probability produced by the hydrogen chloride formed during the chlorination. It is doubtful whether the hydrogen chloride acts mechanically, or really first forms a compound with the liquid cyanide which then breaks up yielding hydrogen chloride and the solid compound. Sulphuric acid does not cause polymerisation. Both the liquid and solid nitriles are converted into α-dichloropropionic acid when heated with moderately strong sulphuric acid. Alcoholic ammonia at 95° converts the solid cyanide into α-dichloropropionamide. Nitrous anhydride has no action on it. When treated with alcohol, zinc and acetic acid, the solid cyanide yields *triethyl cyanuride*, $C_3N_3Et_3$. This substance crystallises in long, hexagonal

prisms, melts at 29°, volatilises at ordinary temperatures, and boils at 193—195°. Its vapour-density corresponds with the formula, $C_9H_{15}N_3$. It is easily soluble in alcohol, ether, and chloroform, sparingly in water, and has an odour resembling that of opium. The aqueous solution is neutral, has a burning taste, and becomes milky when slightly warmed. It is easily soluble in strong hydrochloric acid, and this solution yields a platinochloride. When heated with hydrochloric acid, the cyanuride is decomposed into ammonia and propionic acid.

E. v. Meyer has lately shown (this vol., p. 364) that the compound which has hitherto been called cyanethine is not really a cyanuric compound, but contains an amido-nitrogen-atom. It is therefore probable that the above compound is the true cyanuric compound, and the original compound would then be tri-dichlorethyl cyanuride, $CCl_2Me\cdot C\begin{matrix}<\\<\end{matrix}\begin{matrix}N:C(CCl_2Me)\\N\cdot C(CCl_2Me)\end{matrix}\begin{matrix}>\\>\end{matrix}N$. The yield of the non-chlorinated compound was only about one-third of that theoretically possible. When, in the reduction experiment, the alcohol is mixed with water, a *base*, $C_9H_{16}N_2$, is obtained. This crystallises in silky needles or plates, melts at 111°, boils at 273°, but is not volatile in steam. It has an intensely bitter taste, is readily soluble in alcohol, ether, and chloroform, sparingly in water. Its aqueous solution is strongly alkaline, and it is a monacid base. Its *hydrochloride* forms colourless needles, its *platinochloride* doubly refractive orange crystals; and its *silver-derivative* white flocks. L. T. T.

Action of Acids on Thiocyanic Acid. By P. Klason (*J. pr. Chem.* [2], **36**, 57—64).—It is generally stated that thiocyanic acid is decomposed by acids, yielding either perthiocyanic acid and hydrocyanic acid or carbon oxychloride. The author finds, however, that often, under the action of acids, it yields dithiocarbamic acid, its anhydride or bisulphide. When a strong solution of thiocyanic acid contains little or no mineral acid, it is decomposed into perthiocyanic and hydrocyanic acids. A dilute solution is stable either with or without mineral acid. A strong solution in the presence of a large excess of hydrochloric acid gives off carbon oxysulphide, carbonic anhydride, and a little carbon bisulphide, whilst thiocarbamic bisulphide, $S_2(CS\cdot NH_2)_2$, is formed. The same compound is produced when hydrogen sulphide is passed into a solution of thiocyanic acid. If sulphuric acid is substituted for hydrochloric acid, carbon oxysulphide is evolved, and a mixture of dithiocarbamic anhydride, $S(CS\cdot NH_2)_2$, and thiocarbamic bisulphide is produced. When warmed with water, these substances yield sulphur, carbon bisulphide and ammonium thiocyanate. With aniline, monophenylthiocarbamide and its thiocyanate, diphenylthiocarbamide, ammonium thiocyanate, sulphur, and hydrogen sulphide are formed.

Dry hydrogen chloride has scarcely any action on dry potassium thiocyanate, but if the salt be moist, *thiocarbamic chloride*, $Cl\cdot CS\cdot NH_2$, is formed. This is a white, crystalline substance which volatilises without fusing. It dissolves in water, the solution containing hydrochloric and thiocyanic acids in molecular proportion. L. T. T.

Crystalline Form of Quercin. By C. Friedel (*Compt. rend.*, **105**, 95—96).—The crystals were prepared by Vincent and Delachanal (this vol., p. 909), and are very brilliant, anhydrous, monoclinic prisms the dominant faces being m, and the other faces p and $b^{\frac{1}{2}}$, the latter sometimes truncating the edges mp, sometimes being so largely developed that the base of the prism almost disappears. The following measurements were made: mm, 116° 5′; mg, 31° 57·5′; $pb^{\frac{1}{2}}$, 44° 11′; pm 75° 47′; $mb^{\frac{1}{2}}$, 60° 2′; $b^{\frac{1}{2}}b^{\frac{1}{2}}$, 75° 2′. From these numbers it follows that—

$$D\dot{h} : D\dot{i} : \dot{h} = 0{\cdot}5526 : 1 : 0{\cdot}2125,$$
$$\dot{b} : \dot{h} = 5{\cdot}376.$$

The inclination of the edge h to the inclined diagonal is 62° 21′, and the angle of the base is 57° 50′. Extinction takes place along the plane g^{1}, which is not parallel with the edges mm but makes with them an angle of about 30°. C. H. B.

Comparative Sweetness of Cane- and Starch-sugar. By T. Schmidt (*Bied. Centr.*, 1887, 504).—Experiments proved that 1·53 parts of pure grape-sugar was as sweet as 1 part of pure beet- or cane-sugar. E. W. P.

Decomposition of Saccharose by Boiling with Lime. By W. Niedschlag (*Bied. Centr.*, 1887, 488—489).—As it is a known fact that the yield of crystalline saccharose is less after the crude sugar has been boiled with lime, 250 grams of saccharose were dissolved in 1500 c.c. water, 250 grams slaked lime added, and the whole boiled for 21 days, the result was that most of the sugar was decomposed, and a non-crystalline calcium salt formed containing 20·5 per cent. calcium. Another experiment made for 24 hours with lime, strontia, and baryta, when a water-bath was used, and air excluded, and carbonic anhydride passed in, showed that here again the sugar was decomposed but not to the same extent.

E. W. P.

Substituted Methylenediamines. By A. Ehrenberg (*J. pr. Chem.* [2], **36**, 117—131).—Kolotoff, by the action of trioxymethylene on diethylamine, obtained tetrethylmethylenediamine: this base and its lower homologue could not be prepared by Hofmann's reaction, employing methylene iodide and the corresponding secondary monamine, owing to the fact that the salts of the methylenediamines are extremely unstable, and decompose into trioxymethylene and the hydriodide of the base originally employed. Tetramethylmethylenediamine also could not be obtained by Kolotoff's reaction, but higher homologues were prepared by its means.

Tetrethylmethylenediamine dissolves to the extent of 1 part in 10 parts of water, and on treatment with dilute acids, with perfectly dry hydrogen chloride, and with alcoholic solutions of platinic chloride and of oxalic acid, yields the corresponding salts of diethylamine, whilst prolonged boiling with moist ethyl iodide converts it into tetrethylammonium iodide. When dry carbon bisulphide is added to the dry

base, a molecular compound, $CH_2N_2Et_4,CS_2$, is obtained, which boils at 130—140° with decomposition; if, however, the materials are not quite anhydrous, diethylamine diethyldithiocarbamate is formed.

Tetrapropylmethylenediamine, $CH_2:N_2Pr_4$, is formed when trioxymethylene is heated with the calculated quantity of dipropylamine. It boils at 215—225° with slight decomposition, does not solidify in a freezing mixture of ice and salt, is sparingly soluble in water, readily soluble in alcohol, ether, and chloroform, and yields salts with platinic chloride, gold chloride, and trinitrophenol, which, however, could not be obtained in a state suitable for analysis.

Tetrisobutylmethylenediamine, $CH_2:N_2(C_4H_9)_4$, prepared in a manner similar to the preceding compound, boils at 245—255° with slight decomposition. The *platinochloride*, $C_{17}H_{38}N_2,H_2PtCl_6$, is a fawn-coloured, crystalline powder, melts at 196—198° with decomposition, and when heated to boiling in aqueous solution decomposes into the platinochloride of diisobutylamine. The *aurochloride* is a yellow, crystalline powder, and melts at 185—195° with decomposition. With dry carbon bisulphide, the base forms a molecular compound, $C_{17}H_{38}N_2,CS_2$, which on standing crystallises in large scales, melts at 54°, and in solution stains the skin yellow.

Dipiperidylmethane, $CH_2(NC_5H_{10})_2$, obtained in like manner from piperidine, boils at 230° without decomposition, has a sharp peppermint-like odour, and on treatment with aqueous acids decomposes into trioxymethylene and piperidine. Perfectly dry hydrogen chloride converts the dry base, dissolved in light petroleum, into the hydrochloride if the action is continued only for a short time: this is a white powder which, when separated and dried in an atmosphere free from moisture, contains an amount of hydrogen chloride intermediate between 1 and 2 mols. HCl; the continued action of the gas, however, results in the formation of piperidine hydrochloride. A molecular compound, $C_{11}H_{22}N_2,CS_2$, is obtained on the addition of dry carbon bisulphide to the dry base; this melts at 58°, is soluble in alcohol and ether, insoluble in water, and on treatment with iodine in alcoholic solution is converted into piperidylthiuram bisulphide, $(CS\cdot NC_5H_{10})_2S_2$, which melts at 130°, and is soluble in alcohol and ether, insoluble in water. Moist carbon bisulphide converts the base into piperidine piperidyldithiocarbamate melting at 174°.

Dipiperidylphenylmethane, $CHPh(NC_5H_{10})_2$, has been prepared by Klotz by the action of benzaldehyde on piperidine. It crystallises from alcohol in large, flat needles, melts at 78—79°, and is extremely soluble in benzene, carbon bisulphide, ether, chloroform, toluene, and light petroleum. On distillation in a vacuum, or on exposure to a moist atmosphere, it decomposes with the formation of benzaldehyde.

W. P. W.

Derivatives of Chlorinated Methyl Formate. By W. Hentschel (*J. pr. Chem.* [2], **36**, 99—113).—In the dark, chlorine acts only very slightly on methyl formate even at the boiling point, but in sunlight action is rapid at ordinary temperatures. If the current of chlorine is continued as long as the gas is absorbed, *trichloromethyl chloroformate*, $Cl\cdot COO\cdot CCl_3$, is the main product. This boils at 127·5—128°, and has a sp. gr. 1·6525 at 14°. Its vapour-density is 6·636 (air = 1).

When heated much above its boiling point, it is decomposed, yielding carbon oxychloride. It also closely resembles carbon oxychloride in its reactions. With dimethylaniline and benzaldehyde, it yields a green, with dimethylaniline a violet colour-base. With sodium acetate it yields acetic anhydride. Methyl alcohol acts on it to form a liquid boiling at 163—164°, probably impure OMe·COO·CCl_3.

When the chlorination is stopped at an earlier stage, a compound, $C_4H_3Cl_5O_4$, may be obtained. This is a liquid boiling at 108—109°, and having a very irritating odour. Its sp. gr. is 1·4786 at 14° and 1·4741 at 27°, compared with water at the same temperatures. When heated strongly, it decomposes. With water, it yields carbonic anhydride, carbonic oxide, formaldehyde, and hydrochloric acid. With methyl and ethyl alcohol, it yields methylated derivatives which have not yet been isolated. The compound described by Cahours as perchlormethyl chloroformate has probably a more complicated constitution. L. T. T.

Derivatives of Isopropylformamide. By M. Spica (*Gazzetta*, **17**, 168—171).—*Isopropyl chlorocarbonate*, prepared by the action of carbonyl chloride on isopropyl alcohol, is a colourless oil boiling at 94—96°; sp. gr. at 4° = 1·144; it has an irritating odour, is insoluble in water, but soluble in alcohol and ether.

With α-naphthylamine, it yields *isopropyl formonaphthylamide*, $Pr^{\beta}O·CO·NH·C_{10}H_7$, together with α-naphthylamine hydrochloride, of which the former is soluble, the latter insoluble in alcohol. The formonaphthylamide crystallises in long needles melting at 78—79°, of pungent, aromatic taste, soluble in ether and chloroform.

From β-naphthylamine the corresponding *β-derivative* is obtained; it melts at 70°, and resembles the above compound in crystalline form and appearance. V. H. V.

Derivatives of Isopropyl Chlorocarbonate. By M. Spica and G. de Varda (*Gazzetta*, **17**, 165—168).—On passing a current of ammonia into isopropyl chlorocarbonate, *isopropylformamide* is produced together with ammonium chloride; the former is separated from the latter by its solubility in alcohol. The formamide, $Pr^{\beta}O·CONH_2$, thus obtained crystallises in white, slightly deliquescent needles, melting at 36—37°, soluble in most menstrua.

Similarly from aniline and isopropyl chlorocarbonate, the corresponding *phenyl*-derivative is obtained together with aniline hydrochloride; the two substances are separated by fractional crystallisation from aqueous alcohol. The phenylformamide, $Pr^{\beta}O·CONHPh$, crystallises in prismatic needles melting at 42—43°, soluble in alcohol and ether, insoluble in cold water. V. H. V.

Preparation of Valeric Acid. By E. Duclaux (*Compt. rend.*, **105**, 171—173).—The oxidation of amyl alcohol by potassium permanganate should be effected in presence of an excess of alcohol, otherwise the valeric acid first formed is converted into acetic acid, and this is further oxidised to carbonic anhydride and water. It is likewise necessary to keep the liquid cool. Some acetic acid is always

produced, but this is readily removed by taking advantage of the fact that when a dilute solution of the two acids is distilled, almost the whole of the valeric acid is found in the first quarter of the distillate, whilst the acetic acid remains in the retort. This property of valeric acid seems to be independent of its optical properties. C. H. B.

Isomerism in the Crotonic Acid Series. By A. Michael and G. M. Browne (*J. pr. Chem.* [2], **36**, 174—176).—The authors have not succeeded in obtaining a good yield of α-β-dichlorobutyric acid by passing a current of chlorine through a solution of crotonic acid in carbon bisulphide (compare this vol., p. 655), since the greater part of the crotonic acid is not attacked under these conditions. If, however, the solution, cooled in a freezing mixture, is saturated with chlorine, allowed to remain three days, again saturated with the gas, and finally allowed to remain for three days more, a good yield of the dichlorobutyric acid is obtained. On treatment of an alcoholic solution of the acid (1 mol.) with alcoholic potash (2 mols.) in small portions at a time, α-chlor-allocrotonic acid is formed; this crystallises in needles which melt at 67°, and are soluble in water and light petroleum. The *potassium* salt crystallises from water in white, thin tables, from alcohol in slender needles; the *sodium* salt forms small, prismatic needles; the *barium* salt forms slender needles; the *lead* salt forms octahedral crystals, and the *copper* salt crystallises in greenish-blue, concentrically-grouped prisms. Although anticipated by Wislicenus (*loc. cit.*) in the publication of this work, the authors reserve to themselves the right of continuing the research. W. P. W.

Ethyl Acetocyanacetate. By A. Haller and A. Held (*Compt. rend.*, **105**, 115—117).—23 grams of ethyl cyanacetate is dissolved in its own weight of absolute alcohol and mixed with a solution of 4·6 grams of sodium in 60 grams of absolute alcohol; 8 grams of acetic chloride dissolved in 20 grams of ether is then added, and the liquid is heated until the alkaline reaction disappears. The product is evaporated on a water-bath, the residue taken up with water, and treated with ether to remove ethyl cyanacetate. The aqueous solution is then acidified with sulphuric acid, and the ethyl acetocyanacetate is extracted with ether. It is purified by fractionation in a vacuum. The reaction is represented by the equation $2CN{\cdot}CHNa{\cdot}COOEt + AcCl = NaCl + CN{\cdot}CH_2{\cdot}COOEt + CN{\cdot}CNaAc{\cdot}COOEt$.

This reaction affords positive proof of the accuracy of the constitution generally assigned to this compound.

Three methods of preparing ethyl acetocyanacetate are now known, and the product is the same in all three cases. C. H. B.

Thio-derivatives of Ethyl Carbonate. By P. Klason (*Ber.*, **20**, 2384—2385).—When ethyl alcohol is treated with thiophosgene the principal reaction takes place according to the equation $EtOH + CSCl_2 = HCl + EtCl + COS$, but at the same time some *ethyl chlorothiocarbonate*, CSCl·OEt, is formed. This is a colourless oil of very irritating odour, and boils at 136°. Ammonia converts it into xanthogenamide. When sodium ethoxide is substituted for alcohol in

the above reaction, the action follows the equation $OEtNa + CSCl_2 = OEt{\cdot}CS{\cdot}ONa + 2NaCl + Et_2O$. With ethyl hydrosulphide, thiophosgene yields *ethyl chloroperthiocarbonate*, $CSCl{\cdot}SEt$. It is a yellow oil of irritating odour resembling garlic. In a vacuum, it distils at 100°. Its density at 16° is 1·1408. With sodium thioethylate, thiophosgene forms *ethyl perthiocarbonate*, $CS(SEt)_2$, which is a yellow oil boiling at 240°. L. T. T.

Acids from Acetone-chloroform. By C. Willgerodt (*Ber.*, **20**, 2445—2449).—Three acids are derived from acetone-chloroform, namely, acetonic acid, acetonaloxyisobutyric acid, and acetoxyisobutyric acid. To obtain these oxyisobutyric acids, acetone-chloroform is heated directly with water or aqueous solutions of the alkalis; for the preparation of acetonoxyisobutyric acid, 2 mols. of chloroform and 3 mols. of acetone are condensed with 8 mols. of potash; and for acetonoxybutyric acid 1 mol. acetone-chloroform and 1 mol. acetone are required.

Acetonaloxybutyric acid has been described by the author (Abstr., 1883, 177), and more recently by Engel; its *barium* salt can be obtained in a crystalline form by slow evaporation in a vacuum; the *zinc* salt crystallises in aggregates with 1 mol. H_2O, and the *calcium* salt in small pyramids with $1\frac{1}{2}$ mol. H_2O.

Acetonoxyisobutyric acid, $C_7H_{14}O_4$, crystallises with 1 mol. H_2O in the monoclinic system: $a : b : c = 1{\cdot}719 : 1 : 0{\cdot}609$; $\beta = 109° 80'$. Observed faces, $\infty P\infty$, ∞P, $P\infty$. When kept, it slowly effloresces. V. H. V.

Constituents of Rape-seed Oil. By C. L. Reimer and W. Will (*Ber.*, **20**, 2385—2390).—The authors find that this oil contains the glycerides of erucic, behenic, and *rapic* acids. The behenic acid is only present in small quantities. The oil was saponified, and the erucic and rapic acids separated by means of their zinc salts, zinc erucate being very sparingly soluble in boiling ether, *zinc rapate* easily so. The latter salt was recrystallised from alcohol, and then melted at 78°. *Rapic acid*, $C_{18}H_{34}O_3$, is an oil. Its composition seems to point to its being a hydroxyoleic acid, and an isomeride of ricinoleic acid, but unlike this acid, it does not yield sebacylic acid when fused with potash. Under these circumstances it yields stearic acid, and a second crystalline acid, which has not yet been isolated. *Barium*, *calcium*, *magnesium*, and *silver rapates* form flocculent precipitates; the sodium salt is soluble in water and boiling alcohol.

Goldschmiedt has shown that the oil from black mustard seed contains the glycerides of erucic and behenic acids and of another liquid acid, and it is probable that this oil is identical with rape-seed oil.

Trierucin, $C_3H_5(C_{22}H_{21}O_2)_3$, was obtained by heating dierucin (this vol., p. 233) and erucic acid together at 300°. It is crystalline, melts at 31°, and is soluble in ether and benzene, sparingly so in alcohol. When warmed with nitric acid and sodium nitrite, it is converted into the isomeric tribrassidin. L. T. T.

Preparation of Ethyl Cyanomalonate and Ethyl Benzoylcyanacetate. By A. Haller (*Compt. rend.*, **105**, 169—171).—*Ethyl*

cyanomalonate.—22 grams of ethyl cyanacetate is dissolved in its own volume of absolute alcohol and mixed with a solution of 4·6 grams of sodium in 60 grams of absolute alcohol, and about 6 grams of ethyl chlorocarbonate. A rapid action takes place, and the liquid is heated until it is no longer alkaline. The alcohol is then distilled off, the residue dissolved in water, the unaltered ethyl cyanacetate is removed, and the liquid allowed to evaporate spontaneously. It yields slender needles of the composition $CN\cdot CNa(COOEt)_2$, and when the aqueous solution of this compound is acidified with sulphuric acid, ethyl cyanomalonate is liberated and can be extracted with ether.

Ethyl benzoylcyanacetate is obtained in a similar manner, 1 mol. proportion of benzoic chloride being used for each molecular proportion of ethyl cyanacetate taken.

The action of ethyl iodide on the silver-derivative of ethyl cyanacetate yields a liquid which has an odour of carbylamine, and is in all probability ethyl ethylisocyanacetate. C. H. B.

Action of Ammonia on Ethyl Bromosuccinate. By G. Koerner and A. Menozzi (*Gazzetta*, **17**, 171—176).—Although asparagine is justly regarded as amidosuccinamic acid, yet hitherto it has not been obtained from succinic acid by any direct method of synthesis. With this view, the authors investigated the action of ammonia on ethyl bromosuccinate under various conditions. It is found that both alcoholic and aqueous ammonia in the cold yield fumaramide; if, however, the mixture is heated at 105—110°, a substance isomeric with fumaramide is obtained, which yields barium aspartate when heated with barium hydrate. This compound is probably an imide of aspartic acid, $NH_2\cdot CH<\begin{matrix}CO\cdot NH\\CH_2\cdot CO\end{matrix}>$, as when heated with aqueous ammonia in a sealed tube it takes up a molecule of water, and is thereby converted into asparagine. This synthetical asparagine resembles the natural substance in crystallising with 1 mol. H_2O, but differs from it in being optically inactive. The crystals are holohedral, with hemihedric faces. V. H. V.

Ethyl Succinimidoacetate and Camphorimidoacetate. By A. Haller and G. Arth (*Compt. rend.*, **105**, 280—283).—Succinimide (1 mol.) is dissolved in absolute alcohol, and mixed with sodium ethoxide (1 mol.) and ethyl monochloracetate (1 mol.), and the mixture heated until the alkaline reaction disappears. The alcohol is then driven off, the residue allowed to crystallise and the product purified by repeated crystallisation from ether. *Ethyl succinimidoacetate*, $<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>N\cdot CH_2\cdot COOEt$, is thus obtained in slender needles, very soluble in water, alcohol, and ether. They melt at 66·5°, and remain superfused at the ordinary temperature.

Ethyl camphorimidoacetate, $C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot COOEt$, is obtained in a similar manner, and crystallises from alcohol in large transparent crystals, which melt at 86°, and are soluble in ether.

When ethyl succinimidoacetate dissolved in absolute alcohol is

mixed with an equivalent quantity of metallic sodium also dissolved in alcohol, a gelatinous mass is precipitated, which, after being dried in a vacuum, is very hygroscopic, and dissolves completely in water. The percentage of sodium agrees fairly well with the formula $<^{CH_2\cdot CO}_{CH_2\cdot CO}>N\cdot CHNa\cdot COOEt$, hence it would seem that the presence of the two CO-groups confers acidic functions on the CH_2-group, although they are separated by the nitrogen-atom. C. H. B.

Action of Carbamide on the Chloralcyanhydrins. By A. Pinner and J. Lifschütz (*Ber.*, **20**, 2345—2351). — When equal weights of chloralcyanhydrin, $CCl_3\cdot CH(OH)\cdot CN$, and carbamide are heated together at 90° and lastly at 110°, *trichlorethylidenediureïde*, $CCl_3\cdot CH(NH\cdot CO\cdot NH_2)_2$, is formed. This crystallises in white needles, insoluble in the usual solvents, and decomposes at a high temperature without previous fusion. Biuret and cyanuric acid are also formed, but are probably secondary products due to the action of the liberated hydrogen chloride on carbamide.

When butyrochloral-cyanhydrin and carbamide are heated together at 100—105°, and finally at 120°, two compounds, $C_6H_8Cl_3N_3O_2$ and $C_5H_7ClN_2O_2$, are formed. The former crystallises in small needles, easily soluble in alcohol, sparingly in water; when heated strongly, it is decomposed without previous fusion. It is probably *butyrochloral-biuret*, $CHClMe\cdot CCl_2\cdot CH : (N_2H_2C_2O_2) : NH$. The second compound is *chlorocrotonylcarbamide*, $CHMe : CCl\cdot CO\cdot NH\cdot CO\cdot NH_2$. It appears to be dimorphic, crystallising sometimes in rhombic plates, melting at 224—225°, easily soluble in alcohol, sparingly in water, and sometimes in flat prisms easily soluble in water; the latter melt at 194°, but the re-solidified mass when again heated melts at 209°. When heated above 224°, both modifications of this carbamide evolve hydrochloric acid and yield *ethylidenemetapyrazolone*, $CHMe : C<^{CO\cdot NH}_{NH\cdot CO}>$. This substance crystallises in pale grey needles easily soluble in boiling water. When strongly heated it decomposes without previous fusion.

Besides these compounds, a small quantity of an easily soluble substance crystallising in rhombic prisms was formed. This has not yet been obtained in a pure state. L. T. T.

Behaviour of Furfuraldehyde in the Animal Organism. By M. Jaffé and R. Cohn (*Ber.*, **20**, 2311—2317).—Furfuraldehyde was given to dogs in daily amounts of 5 to 6 grams without producing any appearance of poisoning. In the case of rabbits, the action was much more marked. In the urine of the animals experimented on, the following compounds were found :—Pyromucic acid, pyromykuric acid, and a glycocine compound of furfuracrylic acid.

Pyromykuric acid (*glycocine pyromucate*), $C_7H_7NO_4$, separates from the ethereal extract of the urine in crystalline crusts; it crystallises from water in colourless, transparent prisms, resembling hippuric acid, and melts at 165°. The *barium salt*, $(C_7H_6NO_4)_2Ba + 1\frac{1}{2}H_2O$, is precipitated by alcohol from its concentrated aqueous solution in plates

of a silvery lustre; when boiled with baryta-water, it is decomposed quantitatively into pyromucic acid and glycocine.

Pyromykuric acid carbamide, $C_7H_7NO_4{\cdot}CO(NH_2)_2$, occurs in large quantities in the urine of dogs fed with meat. It crystallises from benzene in groups of colourless needles melting at 120°; it is very readily soluble in water and alcohol, sparingly in ether. When heated with barium carbonate, it decomposes into pyromykuric acid and urea.

Furfuracryluric acid (*furfuracryl-glycocine*), $C_9H_9NO_4$, is obtained in largest amount when dogs are fed with bread, and the furfuraldehyde applied (in 7 per cent. solution) subcutaneously. It forms colourless needles melting at 213—215°, very sparingly soluble in water, rather readily soluble in alcohol. The *silver salt* forms colourless, microscopic needles. When boiled for six to eight hours with strong baryta-water, glycocine and furfuracrylic acid are formed. The latter melts at 140° (not 135°). N. H. M.

Isomeride of Benzene. By G. Griner (*Compt. rend.*, **105**, 283).—Cuprous acetylide is mixed with an alkaline solution of potassium ferricyanide and the mixture is distilled. A solid compound passes over with the water, and is separated, dried, and redistilled. It melts at 64°, and boils at 129—130°; vapour-density 2·81. The formula of the compound is C_6H_6, and it is an isomeride of benzene. It behaves as an unsaturated compound, and in presence of carbon bisulphide combines with four atoms of bromine, forming a crystalline compound which melts at 44°. It does not react with ammoniocuprous chloride, and therefore is not acetylenic in character.

C. H. B.

Action of Cyanuric Chloride and Chlorocyanuric Diamide on Phenols of the Higher Series. By R. Otto (*Ber.*, **20**, 2236—2240).—*Triparanitrophenyl cyanurate*, $(C_6H_4{\cdot}NO_2)_3C_3N_3O_3$, is obtained by adding 1 gram of phenyl cyanurate in very small quantities to 8 c.c. of well-cooled fuming nitric acid. Water is gradually added, and the yellowish-white flakes which separate crystallised from glacial acetic acid. It forms pale-yellow plates melting at 194°. The yield is almost quantitative. When heated with hydrochloric acid for several hours, it is converted into cyanuric acid and paranitrophenol.

Triorthocresyl cyanurate, $(C_6H_4Me)_3C_3N_3O_3$, is prepared by adding sodium to an excess of fused orthocresol, and then the calculated amount of cyanuric chloride. The product is warmed several times with dilute aqueous soda and washed with water. It crystallises in long, pale-yellow needles, melting at 152°, insoluble in water, sparingly soluble in alcohol, readily in ether and glacial acetic acid. The *meta-derivative* resembles the ortho-compound; it crystallises from glacial acetic acid in almost white, microscopic needles which melt at 225°. It is very sparingly soluble in ether and alcohol. The *para-compound* crystallises from a mixture of alcohol and glacial acetic acid in white, matted needles of a silky lustre; it melts at 207° and dissolves sparingly in alcohol and ether.

Trieugenyl cyanurate, $(C_3H_5{\cdot}C_6H_3{\cdot}OH)_3C_3N_3O_3$, is obtained by the action of cyanuric chloride (1 mol.) on the sodium salt of eugenol (3 mols.) in presence of an excess of the phenol as a yellow, oily sub-

stance which solidifies when kept. It crystallises in pale-yellow, microscopic plates, insoluble in cold water, sparingly soluble in ether and alcohol, readily in glacial acetic acid. It melts at 122°.

Trithymyl cyanurate, $(C_6H_3MePr)_3C_3N_3O_3$, resembles trieugenyl cyanurate. It separates from alcohol as a pale-yellow, crystalline powder melting at 151°. It dissolves readily in alcohol and glacial acetic acid, sparingly in water.

α-Trinaphthyl cyanurate, $(C_{10}H_7)_3C_3N_3O_3$, is a greenish-yellow powder, sparingly soluble in hot water, alcohol, and ether, more soluble in glacial acetic acid, benzene, and chloroform; it separates from its solutions in flakes which have no constant melting point, but decompose between 160° and 225°.

β-Trinaphthyl cyanurate is a sparingly soluble, light grey powder which decomposes at 220°.

An excess of sodium phenoxide reacts with chlorocyanuric diamide in presence of phenol, with formation of phenyl cyanurate. When sodium phenoxide and the diamide are employed in molecular proportions *phenylammeline*, $C_3N_3(NH_2)_2(OPh)$, is obtained. This forms an almost white crystalline powder melting at 245°; it is sparingly soluble in ether and alcohol, more soluble in dilute alcohol. When boiled with potash (2 mols.), it is converted into ammelide.

The cresols react with chlorocyanuric diamide, yielding *cresylammelines*, $C_{10}H_{11}ON_5$; the *ortho-compound* is a white, crystalline substance which melts at 225°. N. H. M.

Nitrochlorotoluenes and Chlorotoluidines. By M. Hönig (*Ber.*, **20**, 2417—2420).—By the nitration of orthochlorotoluene, besides metanitro-orthochlorotoluene (Abstr., 1886, 1022) a second nitro-derivative is formed which, when reduced with zinc and hydrochloric acid, yields a liquid chlorotoluidine. The latter forms a chloracetotoluide which crystallises in needles and melts at 136°. After purification by conversion into this toluide, the chlorotoluidine was digested with alcoholic soda and zinc-dust, when orthotoluidine was obtained. The original nitro-derivative must therefore be *orthonitro-orthochlorotoluene*, $NO_2{\cdot}C_6H_3MeCl$ [Me : Cl : NO_2 = 1 : 2 : 5].

Metanitrometachlorotoluene, $C_6H_3MeCl{\cdot}NO_2$[Me : Cl : NO_2 = 1 : 3 : 5], was prepared by removing the amido-group from metadinitroparatoluidine by Staedel's reaction, reducing the metadinitrotoluene thus obtained by means of ammonium sulphide to metanitrometatoluidine, and then, by means of Sandmeyer's reaction, displacing the amido-group in the latter compound by chlorine. It crystallises in yellow needles soluble in alcohol, distils in a current of steam, and melts at 55°. *Metachlorometatoluidine* is a basic oil and boils at 242° under 730 mm. pressure. Its *hydrochloride* and *nitrate* are crystalline; its *aceto-derivative* is soluble in boiling water, crystallises in needles, and melts at 146°.

By the nitration of parachlorotoluene with fuming nitric acid, besides the two mononitro-derivatives, *orthometadinitrochlorotoluene*, $C_6H_3ClMe(NO_2)_2$ [Me : NO_2 : NO_2 : Cl = 1 : 2 : 3 : 4], melting at 76°, is formed. The corresponding diamine hydrochloride gives no quinone with oxidising agents, nor colour reaction with nitrous acid and diazo-

benzene, but with benzaldehyde hydrogen chloride is evolved, showing the correctness of the above formula. This compound is soluble in alkalis. When orthonitroparachlorotoluene is treated with fuming nitric and sulphuric acids, it yields the compound $C_6H_2MeCl(NO_2)_2$ [Me : NO_2 : Cl : NO_2 = 1 : 2 : 4 : 6], melting at 101°. Metanitroparachlorotoluene with fuming nitric acid yields $C_6H_2MeCl(NO_2)_2$ [Me : NO_2: Cl : NO_2 = 1 : 3 : 4 : 5], which melts at 48°.

L. T. T.

Orthocyanotoluene. By S. Gabriel and R. Otto (*Ber.*, **20**, 2222—2224).—*Orthocyanobenzyl chloride*, $CN{\cdot}C_6H_4{\cdot}CH_2Cl$, is prepared by passing dry chlorine into 100 grams of almost boiling orthocyanotoluene until there is an increase in the weight of about 30 grams; if the product is left over night in a dish, in the morning it will have solidified to a mass of crystals of a vitreous lustre. The adhering liquid is removed by suction, and the crystals washed with cold alcohol. It dissolves in hot water, more readily in hot alcohol, melts at 60—61·5°, and boils at 252° under 758·5 mm. pressure; the vapour is extremely irritating to the eyes and nose. The crystals are monoclinic; $a : b : c = 0{\cdot}7775 : 1 : 0{\cdot}2939$; $\beta = 60° 2'$.

Orthocyanobenzyl cyanide, $CN{\cdot}C_6H_4{\cdot}CN_2{\cdot}CN$, is obtained by adding 30 grams of the chloride to a solution of 15 grams of potassium cyanide (96—98 per cent.) in 60 c.c. of water and 300 c.c. of alcohol, and heating the whole for 45 minutes in a reflux apparatus. Two-thirds of the alcohol is then distilled off, and the residue poured into 500 c.c. of water. The crystals so obtained are freed from adhering liquid by suction, washed and dried. It crystallises from alcohol in colourless plates which melt at 81° and dissolve readily in the usual solvents.

N. H. M.

Oxidation of the Homologues of Phenol. By B. Heymann and W. Koenigs (*Ber.*, **20**, 2390—2397).—The authors have now extended their experiments on this subject (see Abstr., 1886, 542, and this vol., p. 241) to dihydric phenols.

When thymoquinol tetrapotassium diphosphate, $K_4(C_{10}H_{12})P_2O_8$, was oxidised by means of potassium permanganate, paradihydroxyterephthalic acid (Baeyer, Abstr., 1886, 445) was obtained. The yield was very small, but the same acid was obtained with a better yield by the oxidation of paraxyloquinol tetrapotassium diphosphate, $K_4(C_8H_8)P_2O_8$, which contains no large side-chain detrimental to ready oxidation. Paraxyloquinone is best prepared by dissolving 100 grams of commercial pseudocumidine, $C_6H_2Me_3{\cdot}NH_2$, in two litres of water containing 800 grams of strong sulphuric acid, and treating this solution with excess of manganic peroxide. The reduction to paraxyloquinol, $C_6H_2Me_2(OH)_2$, is best carried out by means of zinc-dust and acetic acid.

In their last communication on this subject, the authors described an acid isomeric with parapropenylsalicylic acid. Several salts of this acid are now described, but its constitution has not yet been determined.

L. T. T.

Constitution of Chlor- and Brom-anilic Acid. By A. Hantzsch and K. Schniter (*Ber.*, **20**, 2279—2282; compare this vol., p. 719).—When meta- and para-dichloroquinone are brominated, they yield the same dichlorodibromoquinone [$O_2 : Cl_2 : Br_2 = 1 : 4 : 2 : 6 : 3 : 5$]. When the quinone is reduced by means of hydroxylamine, a quinol is formed, melting at 233·5—234°. The acetyl-derivative melts at 268—270°. (Compare also Levy, Abstr., 1885, 1210.) N. H. M.

Preparation of Quinones: Halogen-derivatives of Toluquinone. By K. Schniter (*Ber.*, **20**, 2282—2288).—Toluquinone is prepared in the following manner:—20 grams of orthotoluidine is dissolved in 600 c.c. of water and 160 grams of sulphuric acid, the solution cooled to 10—15°, and treated for an hour with 20 grams of very finely powdered potassium dichromate. The whole is left over night and is then treated with 33 grams of potassium dichromate. The product is extracted with ether, the extract dried and the ether distilled off. The almost pure and dry quinone so obtained weighs about 19 grams. In a similar manner 19 grams of quinone was obtained from 20 grams of aniline.

Chlorotoluquinol, $C_6H_2MeCl(OH)_2$, is formed when finely powdered toluquinone is kept in contact with strong hydrochloric acid for 12 to 24 hours. The product is crystallised first from light petroleum, and then from water in presence of sulphurous acid. It separates in needles or plates which melt at 175° with decomposition; it dissolves sparingly in light petroleum, readily in ether, chloroform, and in hot water, and becomes oxidised when exposed to air.

Bromotoluquinol, $C_6H_2MeBr(OH)_2$, is prepared in a manner similar to the chloro-derivative. It crystallises from water in lustrous plates melting at 160°.

Chlorotoluquinone, $C_6H_2MeClO_2$, is obtained by distilling the quinol with a solution of ferric chloride, or by oxidising it with chromic mixture. The product contains higher substituted quinones which could not be removed; it melts constantly at 105°, dissolves readily in ether, chloroform, and alcohol, sparingly in hot water. The *bromo-derivative* crystallises from alcohol in broad, yellow crystals, melting at 105°; it could not be obtained pure.

Chlorobromotoluquinol, $C_6HMeClBr(OH)_2$, is formed by the union of chlorotoluquinone and hydrogen bromide. It is soluble in benzene and chloroform, and dissolves very readily in ether and alcohol, crystallising from the latter solvent with 1 mol. H_2O. It dissolves slowly in water and in light petroleum. The anhydrous compound melts at 123°.

Bromochlorotoluquinol, $C_6MeBrCl(OH)_2 + H_2O$, is prepared by the action of hydrogen chloride on bromotoluquinone. It crystallises from hot water in stellate groups of needles melting at 120—121°. Unlike its isomeride, it retains its water of crystallisation when kept over sulphuric acid.

Chlorobromotoluquinone, $C_6HMeClBrO_2$, obtained by oxidising chlorobromotoluquinol, crystallises from alcohol in needles melting at 109—111°; it dissolves very readily in ether, benzene, and chloroform, but is scarcely soluble in water.

Bromochlorotoluquinone, $C_6HMeBrClO_2$, prepared from bromochlorotoluquinol, crystallises from alcohol in lustrous, yellow needles which melt at 150°.

Monochlorotoluquinone reacts with hydrogen chloride with formation of dichlorotoluquinol melting at 120—121° (Claus and Schweitzer, Abstr., 1886, 614). The reaction is accompanied with considerable rise of temperature. N. H. M.

Formation of Primary Amines from the Corresponding Halogen-derivatives. By S. Gabriel (*Ber.*, **20**, 2224—2236).—*Ethylenediphthalimide*, $C_8H_4O_2:N\cdot CH_2\cdot CH\cdot N:C_8H_4O_2$, is prepared by heating potassium phthalimide (10 grams) with ethylene bromide (12 grams) for two hours at 200°, and boiling the product with water containing a little caustic soda. The insoluble, oily substance thus obtained solidifies on cooling, and is boiled with 50 c.c. of alcohol. When cold, the ethylenediphthalimide is collected and crystallised from glacial acetic acid, from which it separates in long, lustrous needles melting at 232°. The chief product of the reaction is *bromethylphthalimide*, $C_8H_4O_2:N\cdot C_2H_4Br$, which crystallises from water, in which it is very sparingly soluble, in long needles melting at 82—83·5°. When ethylenediphthalimide is heated with 3 parts of fuming hydrochloric acid at 200°, it is converted into ethylenediamine and phthalic acid.

Benzylphthalimide, $C_8H_4O_2:N\cdot CH_2Ph$, is obtained by heating potassium phthalimide (3 parts) and benzoic chloride (2 parts) for two hours at 170 to 180°; it crystallises from alcohol in long needles melting at 115—116°. When heated with fuming hydrochloric acid at 200°, it is decomposed into benzylamine and phthalic acid.

Orthonitrobenzylphthalimide, $C_8H_4O_2:N\cdot CH_2\cdot C_6H_4\cdot NO_2$, is prepared by rubbing 37 grams of potassium phthalimide with 31·5 grams of orthonitrobenzoic chloride, shaking the mixture loosely into a glass, and heating it for half an hour in a water-bath; the temperature is then slowly raised (during two hours) to 150° in an oil-bath. The product is treated with water containing soda, heated in a water-bath, filtered, and extracted with boiling alcohol. It crystallises in lustrous, well-formed prisms, which melt at 217·5—219°; it dissolves sparingly in boiling glacial acetic acid, less so in hot alcohol.

Orthonitrobenzylamine, $NH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$, is obtained by heating the above imide with fuming hydrochloric acid (4 parts) at 190° to 200°. It is an oily substance, readily soluble in water; when exposed to air, it absorbs carbonic anhydride and becomes solid. The *hydrochloride* crystallises in lustrous needles an inch long, readily soluble in water; the *platinochloride*, $(C_7H_8N_2O_2)_2,H_2PtCl_6 + 2H_2O$, crystallises in amber-coloured prisms. The *acetyl-derivative* crystallises in colourless needles melting at 97—99°.

Orthamidobenzylamine, $NH_2\cdot C_6H_4\cdot CH_2\cdot NH_2$, prepared by reducing the nitro-compound with tin and hydrochloric acid, forms a crystalline mass, which dissolves readily in water and distils slowly with steam. The *primary hydrochloride*, $C_7H_{10}N_2,HCl$, and the *secondary hydrochloride*, both crystallise in colourless needles; the *picrate* forms lemon-coloured needles. The *diacetyl-compound* crystallises from

benzene in needles melting at 136—137°; it is readily soluble in warm water, sparingly in ether.

Orthocyanobenzylphthalimide, $C_8H_4O_2 : N\cdot CH_2\cdot C_6H_4\cdot CN$, is prepared by slowly heating an intimate mixture of orthocyanobenzoic chloride (7 parts) and potassium phthalimide (9 parts) from 100° up to 120° for half an hour. The product is extracted with boiling water, and the undissolved portion dissolved in boiling glacial acetic acid, from which it separates in long prisms melting at 181—182°.

Orthocyanobenzylamine, $CN\cdot C_6H_4\cdot CH_2\cdot NH_2$, is formed when the above phthalimide compound is digested with fuming hydrochloric acid. It is a colourless oil, which crystallises when rubbed, and dissolves readily in water. The hydrochloride (with 1 mol. H_2O) crystallises in lustrous needles; the *picrate* is obtained as a sparingly soluble, yellow, crystalline precipitate. When the acid solution of the hydrochloride is treated with sodium nitrite, nitrosophthalimidine is formed.

Orthochloromethylbenzamide, $CH_2Cl\cdot C_6H_4\cdot CONH_2$, is obtained by heating a solution of orthocyanobenzoic chloride in strong sulphuric acid at 80° to 90°; the product is poured into water and filtered; the crystals are then washed and dried over sulphuric acid. It is insoluble in cold water, and is decomposed by boiling with water or alcohol with formation of phthalide and ammonium chloride. When slowly heated until a temperature of 150° to 160° is reached, dissolved in warm water and treated with potash, *pseudophthalimidine*, C_8H_7NO, is obtained as a brownish oil, having a peculiar odour. The *picrate* forms a sparingly soluble, yellow, crystalline powder; the *platinochloride* crystallises in orange-coloured, flat needles (with 2 mols. H_2O). When distilled, the base decomposes with evolution of ammonia; and if boiled with a mixture of phosphorus oxychloride and pentachloride, orthochlorobenzoic cyanide is formed. N. H. M.

Action of Dilute Nitric Acid on Substituted Amido-compounds. By L. M. Norton and W. D. Livermore (*Ber.*, **50**, 2268—2274).—*Trinitromethylparatoluidine* is prepared by boiling acetylmethylparatoluidine for 2 to 3 hours with 5 per cent. nitric acid, or for 1 to 2 hours with 10 per cent. nitric acid. It is crystallised several times from alcohol; it melts at 129—130°. When boiled with 4 per cent. aqueous potash, it is converted into Martius' dinitrocresol (*Ber.*, **2**, 207), melting at 82—83°. The constitution of the trinitro-compound is therefore probably $[Me : NO_2 : NMe(NO_2) : NO_2 = 1 : 3 : 4 : 5]$; the compound is possibly identical with that obtained by van Romburgh (*Rec. Trav. Chim.*, 1884, 392), by the action of nitric acid on dimethylparatoluidine. It is also obtained by the action of dilute nitric acid on acetylmethylpropionylparatoluide.

Dinitromethylaniline (m. p. 174·5°) is formed when methylformanilide is boiled with 12½ per cent. nitric acid for 30 minutes. *Methylformanilide* is prepared by heating sodium formanilide with methyl iodide; it melts at 12·5° and boils at 250°.

Methyloxanilide is prepared by adding a concentrated alcoholic solution of oxalic acid to methylaniline mixed with a little alcohol; the precipitate is separated and heated at 160—180° until no more

gas is evolved. It is liquid and boils at 249—251°. When boiled with nitric acid, it is converted into dinitromethylaniline, melting at 176—177°. This, when boiled with aqueous potash, is converted into dinitrophenol [1 : 2 : 4]. (Compare also Abstr., 1885, 1213.)

N. H. M.

Phenyl-derivatives of Ethane. By K. Heúmann and J. Wiernik (*Ber.*, **20**, 2421—2427).—When glycol is heated with dimethylaniline and zinc chloride for some days at 100—120°, *dimethamidophenylethane*, $C_6H_4Et{\cdot}NMe_2$ [Et : NMe_2 = 1 : 4], is formed together with small quantities of hexamethylparaleucaniline. The former crystallises in greyish-blue scales or prisms, easily soluble in alcohol and ether, and melting at 89°. It is soluble in acids, but its salts crystallise with difficulty. Nitrous acid yields *nitrosomethamidophenylethane*, $C_6H_4Et{\cdot}NMe{\cdot}NO$, which crystallises in needles and melts at 162°. When reduced with acetic acid and zinc, the nitrosamine yielded an oil boiling at about 260°, probably a hydrazine base, $C_6H_4Et{\cdot}NMe{\cdot}NH_2$, which gave an *acetyl*-derivative melting at 68°.

Monochlorethylene chloride and dimethylaniline, under like conditions, yield dichlorethylene, *hexamethyltriamidotriphenylethane*, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, and another crystalline compound melting at 84°, the constitution of which has not yet been determined. The former compound is easily soluble in ether, benzene, and acetic acid, sparingly in alcohol, and insoluble in water. With many oxidising agents, it gives greenish colouring matters.

Carbon hexachloride, dimethylaniline, and zinc chloride when heated together yield perchlorethylene and tetramethyldiamidodiphenylmethane; the latter is also formed when perchlorethylene is substituted for carbon hexachloride in this reaction.

L. T. T.

Cumylamine. By H. Goldschmidt and A. Gessner (*Ber.*, **20**, 2413—2416).—Cumylamine was prepared by the reduction of cuminaldoxime with sodium amalgam. It is a colourless, limpid liquid boiling at 225—227° under 724 mm. pressure, and not at 280°, as usually stated. *Acetocumylamine*, $C_3H_7{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHAc$, forms micaceous scales soluble in alcohol, ether, and benzene, sparingly in boiling water: it melts at 65°.

Cumylthiocarbamide, $C_3H_7{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$, prepared from cumylamine hydrochloride and potassium thiocyanate, forms colourless scales melting at 110°. It is easily soluble in benzene and in cold water. *Phenylcumylthiocarbamide*, $C_3H_7{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh$, from cumylamine and phenyl thiocyanate, forms microscopic plates soluble in alcohol, benzene, and boiling water, and melting at 106°.

L. T. T.

Orthamidophenyl Mercaptan and its Derivatives. By A. W. Hofmann (*Ber.*, **20**, 2251—2265).—When a small quantity of phenyl mercaptan is dissolved in a strong alcoholic solution of cyanogen, the liquid becomes coloured, and after 10 to 15 minutes a separation of almost colourless, lustrous needles takes place, and in an hour the reaction is finished. Analyses show that the new compound is

formed by simple addition of the elements of cyanogen; it probably has the constitution $C_6H_4<^{N}_{S}>C\cdot C(NH)\cdot NH_2$. It melts at 150°, with evolution of gas, and dissolves in benzene, ether, and alcohol. The *aurochloride*, $C_8H_7N_3S,HAuCl_4$, crystallising in slender needles, and the *platinochloride*, $C_8H_7N_3S,H_2PtCl_6$, were prepared.

Monophenylamidine, $C_6H_4<^{N}_{S}>C\cdot C(NH)\cdot NHPh$, is formed together with the diphenyl-derivative when the amidine is heated with aniline. The reaction is accompanied by an evolution of ammonia, and afterwards of hydrogen cyanide. The product is steam-distilled to remove the excess of aniline; the monophenylamidine remains as a yellow oil which solidifies on cooling, whilst the diphenyl compound is contained in the aqueous solution. Monophenylamidine crystallises in pale-yellow plates which melt at 118° and dissolve in alcohol and ether. The *hydrochloride* forms long needles; the *platinochloride* separates from its solution in small, concentrically-grouped needles; the *aurochloride* crystallises in bright-yellow, rhombic plates.

Diphenylamidine, $C_7H_4NS\cdot C(NPh)\cdot NHPh$, separates in part from the aqueous solution on cooling; the rest is extracted with ether. It crystallises from water in white plates of a silvery lustre which melt at 129°; it dissolves readily in alcohol and ether. The *platinochloride*, $C_{20}H_{15}N_3S,H_2PtCl_6$, crystallises in dark-yellow plates; the *aurochloride*, $C_{20}H_{15}N_3(HAuCl_4)_2$, forms gold-coloured, hair-like needles. Both salts are sparingly soluble.

When the amidine, dissolved in alcohol, is warmed with a few drops of mercaptan, ammonia is evolved and crystals of the oxalyl-compound, $C_{14}H_8N_2S_2$ (*Ber.*, 13, 1228), separate. Alcoholic potash solution decomposes the amidine with evolution of ammonia and formation of the potassium salt of an acid, $C_6H_4<^{N}_{S}>C\cdot COOH$. The *free acid* crystallises in groups of needles readily soluble in alcohol, less soluble in water and in hydrochloric acid. It melts at 108°, with evolution of carbonic anhydride. When the aqueous solution is boiled, the acid decomposes into the methenyl base, $C_6H_4<^{N}_{S}>CH$, and carbonic anhydride.

The preparation of amidophenyl mercaptan is described in detail.

The vapour of amidophenyl mercaptan or its solution is a powerful irritant, causing blisters when in contact with the skin; all its derivatives appear to have this property.

When the aqueous solution of the amyl iodide of the methenyl base, C_7H_5NS, is treated with ammonia, no dye is formed; the same result is obtained with the ethenyl base. When both solutions are mixed and then boiled, a dark-red, resinous mass is obtained which yields splendid, well-formed plates of a green metallic lustre, violet-red in transmitted light; analyses of it point to the formula $C_{25}H_{31}N_2S_2I$. It dissolves in alcohol yielding a deep-red solution which is decolorised by acids; the colour returns on the addition of alcohol or water. In a similar manner, dyes can be prepared from the corresponding naphthyl base (this vol., p. 839), and from a mixture of the phenyl and naphthyl

bases. Experiments with the amyl iodides of quinoline bases and with those of mercaptan-derivatives also gave dyes; these could not be obtained in a crystalline form. N. H. M.

Anisamine. By H. Goldschmidt and N. Polonowska (*Ber.*, **20**, 2407—2413).—Anisamine, $OMe\cdot C_6H_4\cdot CH_2\cdot NH_2$, is easily obtained by the reduction of anisaldoxime by sodium amalgam. The free base is a colourless oil, soluble in water, and boils at 234—235°. When exposed to the air, it absorbs carbonic anhydride and forms white needles melting at 110°. This substance, which is probably *anisylamine anisylcarbamate*, is what Cannizzaro described (*Annalen*, **117**, 240) as the free base. The *hydrochloride*, $C_8H_{11}NO,HCl$, yields transparent prisms melting at 231°, the *mercurochloride*, $C_8H_{11}NO,HHgCl_3 + H_2O$, in silvery scales which lose water at 130° and melt with decomposition at 200°.

Acetanisamine (*anisylacetamide*), $OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_2H_3O$, crystallises in needles melting at 96°; *anisylcarbamide*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$

in long thin needles melting at 167°; *anisylthiocarbamide*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot CS\cdot NH_2,$$

in transparent needles melting at 95°. *Dianisylthiocarbamide*,

$$CS(NH\cdot CH_2\cdot C_6H_4\cdot OMe)_2,$$

is formed by mixing together anisamine and carbon bisulphide, and boiling the resulting product with alcohol as long as hydrogen sulphide is evolved. It is soluble in alcohol, crystallises in colourless needles, and melts at 149—150°.

When acetanisamine is gradually added to well-cooled strong nitric acid, *metanitracetanisamine*, $OMe\cdot C_6H_3(NO_2)\cdot CH_2\cdot NHAc$ [$CH_2\cdot NHAc : NO_2 : OMe = 1 : 3 : 4$], is formed. This dissolves in alcohol, crystallises in pale-yellow prisms, and melts at 137°. When oxidised with chromic mixture, it yields metanitranisic acid, and small quantities of paranitranisol, $OMe\cdot C_6H_4\cdot NH_2$.

When metanitracetanisamine is treated with tin and hydrochloric acid, *metamidanisamine*, $OMe\cdot C_6H_3(NH_2)\cdot CH_2\cdot NH_2$, is formed. This is a basic oil which absorbs carbonic acid from the air and becomes solid. It is sparingly soluble in ether, and almost non-volatile in steam. The *hydrochloride* forms unstable, colourless needles; the *platinochloride* has the formula

$$[OMe\cdot C_6H_3(NH_2,HCl)\cdot CH_2\cdot NH_2]_2,H_2PtCl_6.$$

Diacetometamidanisamine, $OMe\cdot C_6H_3(NHAc)\cdot CH_2\cdot NHAc$, forms white needles melting at 185°.

Anisaldoxime melts at 61°, and not at 45°, as stated by Westenberger. L. T. T.

Behaviour of Tertiary Amines towards Nitrous Acid. By E. Koch (*Ber.*, **20**, 2459—2461).—Heidlberg has recently described

a compound, believed by him to be a nitroso-derivative of parachlorodimethylaniline (this vol. p. 475). This view, however, is improbable, as in the action of nitrous acid on the tertiary amines the nitroso-grouping takes up the 4 position, which in this case is already occupied. On repeating the experiments, the course of the reaction was found to be different from that described by Heidlberg, in that a nitro-derivative is formed as shown by analysis and the non-production of Liebermann's reaction. Further, the diamine obtained on reduction gives the reaction of a meta-compound. From the mother-liquor of the nitro-compound, a *nitrosamine*, $C_6H_4Cl{\cdot}N(NO)Me$, is obtained crystallising in light-brown needles which melt at 51°; this gives Liebermann's reaction. V. H. V.

Preparation of Phenylhydrazine. By A. Reychler (*Ber.*, **20**, 2463—2464).—In order to avoid the production of diazobenzene chloride in the preparation of phenylhydrazine, the following plan is recommended. Aniline (1 mol.) and potassium carbonate ($\frac{1}{2}$ mol.) are mixed with water and brought into solution by passing in the quantity of sulphurous anhydride required to form aniline sulphite and hydrogen potassium sulphite. The solution thus obtained is added gradually to an aqueous solution of potassium nitrite (1 mol.), carefully neutralised with acetic acid. If the operation is successful, no gas is evolved. The whole is then allowed to remain for two hours, and the precipitate formed is brought into solution by heating on a water-bath; the liquid is acidified with dilute acetic acid, and decolorised by careful addition of dilute hydrochloric acid and zinc-dust. After filtering, adding hydrochloric acid and evaporating the liquid to half its bulk, the phenylhydrazine hydrochloride may be precipitated by concentrated hydrochloric acid. The yield of the crude precipitate is 85·90 per cent. of that required by theory; this is reduced to 65·70 per cent. on purification. V. H. V.

Preparation of Iodobenzene from Phenylhydrazine and Titration of the Latter. By E. v. Meyer (*J. pr. Chem.* [2], **36**, 115—116).—E. Fischer has shown (*Ber.*, **10**, 1335) that hydriodic acid, diazobenzimide, and aniline hydriodide are formed when iodine acts on an excess of phenylhydrazine. The author finds that if the iodine is kept in excess the decomposition takes place according to the equation $N_2H_3Ph + 2I_2 = 3HI + N_2 + PhI$. This reaction may be employed to prepare iodobenzene and to titrate phenylhydrazine. In the latter case, the phenylhydrazine is added to a titrated solution of iodine, and the excess of iodine determined by hyposulphite. The titration of phenylhydrazine may also be effected by iodic acid in the presence of dilute sulphuric acid. L. T. T.

Action of Carbamide on Phenylhydrazine. By A. Pinner (*Ber.*, **20**, 2358—2360).—If carbamide (1 mol.) is heated with two molecular proportions of phenylhydrazine hydrochloride, phenylsemicarbazide, $NHPh{\cdot}NH{\cdot}CO{\cdot}NH_2$ (E. Fischer, Abstr., 1878, 307), is formed. If, however, three or more molecular proportions of the hydrazide are

employed, a new compound, *phenylurazole*, $C_8H_7N_3O_2$, is produced. This crystallises in colourless, glistening scales, easily soluble in boiling alcohol and boiling water, sparingly so in ether. It melts at 262—263°. It is soluble in alkalis, and is reprecipitated from this solution by acids; it does not reduce silver or copper solutions. Its constitution is either $NPh<^{CO\cdot NH}_{NH\cdot CO}>$ or $NPh<^{C(OH):N}_{N:C(OH)}>$, probably the latter. As other hydrazines and amides may yield similar compounds, the author proposes the name *urazoles* for the whole class of derivatives. L. T. T.

Derivatives of Acetylorthamidobenzamide. By A. Weddige (*J. pr. Chem.* [2], **36**, 141—154).—*Ethyl acetylorthamidobenzoate*, $NHAc\cdot C_6H_4\cdot COOEt$, is prepared by the action of acetic anhydride on ethyl orthamidobenzoate, and crystallises from alcohol in nacreous needles, or by slow evaporation in large transparent prims, melts at 61—62°. It is not attacked by alcoholic ammonia at 150—160°, but is converted into anhydroacetylorthamidobenzamide when heated with aqueous ammonia.

Anhydroacetylorthamidobenzamide (Abstr., 1885, 661) can be obtained by heating acetylorthamidobenzamide at 230—240°, by boiling an aqueous solution of the compound for some time, or by dissolving it in aqueous alkalis, and precipitating with an acid. In the last reaction, a salt of the anhydro-compound seems to be at once formed by the action of the alkali with the elimination of the elements of water, since the addition of silver nitrate to the alkaline solution (which could not be crystallised) precipitates a white *silver* salt, $C_9H_7N_2OAg$; whilst long silky needles of the *potassium* salt containing alcohol of crystallisation are obtained, when an alcoholic solution of acetylorthamidobenzamide is treated with alcoholic potash. The anhydro-compound crystallises in white, silky, lustrous needles, melts at 232—233°, and dissolves readily in hot water, from which it separates on cooling in thick prisms with 1 mol. H_2O; in benzene, ether, chloroform, and cold alcohol it is sparingly soluble. The *hydrochloride*, $C_9H_8N_2O,HCl$, crystallises in bright-yellow or white needles, is soluble in hot water, and yields precipitates with various metallic salts. The *methyl* salt, $C_9H_7N_2O\cdot Me$, is formed when either acetylorthamidobenzamide or its anhydro-derivative are heated with methyl iodide and alcoholic potash in a reflux apparatus for two to three hours. It crystallises from water in long silky needles, which melt at 70°, or when anhydrous at 108—109°, and effloresce on exposure to the air. It dissolves readily in alcohol, less readily in ether and benzene, and forms salts with acids: of these the hydrochloride crystallises in small prisms.

Orthamidobenzomethylamide, $NH_2\cdot C_6H_4\cdot CONHMe$, is obtained by the action of an alcoholic solution of methylamine on isatoic acid. It crystallises from benzene in long, thick, yellowish prisms, or occasionally in long thin feathery needles showing a nacreous lustre, melts at 79—80°, and is very readily soluble in alcohol and ether, readily soluble in hot benzene, and soluble in hot water. On treatment with acetic anhydride, the *acetyl*-derivative is obtained; this crystallises in long,

colourless, lustrous prisms, melts at 171—172°, and is sparingly soluble in ether, benzene, and cold alcohol. When boiled with water or aqueous alkalis, or when heated at 200—220° for some time, it is converted into *anhydroacetylorthamidobenzmethylamide*, $C_{10}H_{10}N_2O$, a compound identical with the methyl-derivative of anhydroacetylorthamidobenzamide just described.

Orthomethamidobenzamide, $NMeH\cdot C_6H_4\cdot CONH_2$, is prepared by adding methyl iodide to orthamidobenzamide in alcoholic solution, and precipitating the base from an aqueous solution of the crystalline hydriodide by ammonia. It crystallises in nacreous scales, melts at 159—160°, and dissolves in alcohol yielding a solution fluorescing blue. When heated with acetic anhydride, it is converted into the *acetyl*-derivative, which crystallises in long, white needles, melts at 155°, and is sparingly soluble in benzene, ether, and cold alcohol. If it is heated above its melting point, the *anhydro*-derivative is formed; this crystallises from water in pale-yellow prisms with 3 mols. H_2O, melts at 199° when anhydrous, is very readily soluble in alcohol, and yields a well-crystallised hydrochloride.

Anhydroacetylorthamidobenzamide is regarded as a derivative of a hypothetical base, *quinazoline*, $C_6H_4<\begin{matrix}CH:N\\N:CH\end{matrix}>$, isomeric with cinnoline and quinoxaline, and since its methyl-derivative is identical with the anhydroacetyl-derivative obtained from orthamidobenzmethylamide, it must have either the constitution

$$C_6H_4<\begin{matrix}CO\cdot NH\\N:CMe\end{matrix}>, \text{ or } C_6H_4<\begin{matrix}C(OH):N\\-N:CMe-\end{matrix}>;$$

it is therefore termed *β*-methyl-*δ*-oxyquinazoline. Adopting this nomenclature, anhydroacetyl orthamidobenzmethylamide,

$$C_6H_4<\begin{matrix}CO\cdot NMe\\N:CMe\end{matrix}>,$$

is termed *β*-*γ*-dimethyl-*δ*-pseudoxyquinazoline, and anhydroacetyl orthomethylamidobenzamide, $C_6H_4<\begin{matrix}-CO\cdot N-\\NMe:CMe\end{matrix}>$, is termed *α*-*β*-dimethyl-*δ*-pseudoxyquinazoline. W. P. W.

Derivatives of Benzoylorthamidobenzamide. By M. Körner (*J. pr. Chem.* [2], **36**, 155—165). — *Benzoylorthamidobenzamide*, $NHBz\cdot C_6H_4\cdot CONH_2$, is formed by adding benzoic chloride in small quantities at a time to orthamidobenzamide dissolved in ether. It crystallises from absolute alcohol in long, white, lustrous, matted needles, melts at 218—219°, becomes strongly electrical when rubbed in a mortar, and is insoluble in water, sparingly soluble in all ordinary solvents. Aqueous potash and soda dissolve it on heating, but the solutions on treatment with an acid yield the anhydro-derivative, *β-phenyl-δ-oxyquinazoline*, $C_{14}H_{10}N_2O$ (for nomenclature, compare preceding Abstract). This compound can also be readily obtained by heating the benzoyl-derivative at 250—260° for an hour; it crystal-

lises in pale-yellow microscopic needles, melts at 233—234°, and is insoluble in water, sparingly soluble in benzene, chloroform, and absolute alcohol. It becomes strongly electrical when powdered in a mortar. The *hydrochloride* crystallises from concentrated hydrochloric acid in lustrous, transparent, rhombic tables, and is decomposed by washing with water or treatment with hot alcohol; the *platinochloride*, $(C_{14}H_{10}N_2O)_2,H_2PtCl_6$, crystallises in long brick-red needles.

Benzoylorthamidobenzmethylamide, $C_{15}H_{14}N_2O_2$, is obtained by the action of benzoic chloride on orthamidobenzmethylamide dissolved in ether. It crystallises in large, transparent tables, apparently hexagonal, melts at 181°, and is insoluble in water, sparingly soluble in benzene and absolute alcohol. When heated at 250° for half an hour, it is converted into the anhydro-compound, *β-phenyl-γ-methyl-δ-pseudoxyquinazoline*, $C_6H_4<\begin{matrix}CO\cdot NMe\\N:CPh\end{matrix}>$, which crystallises from alcohol in large scales or prisms, from water in large, lustrous lamellæ, and melts at 130—131°. This compound is identical with that obtained when a mixture of β-phenyl-δ-oxyquinazoline, or benzoyl orthamidobenzamide and potassium hydroxide dissolved in absolute alcohol, is heated to 110°, treated with methyl iodide, and afterwards heated at 120° for six hours.

Acetylorthamidobenzophenylamide, $NHAc\cdot C_6H_4\cdot CONHPh$, is formed by the action of acetic anhydride on orthamidobenzophenylamide, itself obtained by adding aniline in alcoholic solution to isatoic acid. It crystallises in drusy aggregates of long, white needles, melts at 167—168°, and is insoluble in water and ether, readily soluble in benzene, acetic acid, &c. When heated at 210° for some time, it is converted into the anhydro-compound, *β-methyl-γ-phenyl-δ-pseudoxyquinazoline*, $C_6H_4<\begin{matrix}CO\cdot NPh\\N:CMe\end{matrix}>$; this crystallises in large, yellow prisms, melts at 146—147°, and is soluble in absolute alcohol, insoluble in water. W. P. W.

Action of Yellow Ammonium Sulphide on Ketones and Quinones. By C. Willgerodt (*Ber.*, **20**, 2467—2470).—The reaction of yellow ammonium sulphide on ketones and quinones is very variable, depending on the constitution of the compound, the proportion of sulphur in the ammonium sulphide, and the temperature at which the reaction is effected.

Thus in the case of acetone there is formed a *duplodithioacetone*, $(CS_2Me_2)_2$; $a : c = 1 : 0{\cdot}8675$; observed faces, P, $\infty P\infty$, which crystallises in the tetragonal system; it melts at 98°, and boils at 243°, with partial decomposition; it has a characteristic disagreeable odour, is insoluble in water, but soluble in most organic menstrua.

α-Naphthyl methyl ketone, when heated with carbon bisulphide in sealed tubes at 210—230°, yields a compound, $C_{12}H_{11}NO$, crystallising in colourless needles, which melt at 154°, and sublime without decomposition. This compound is isomeric with both amido-α-naphthyl methyl ketone, and α-naphthyl acetoxime; probably it has the composition of a ketone-imide, the formation of which is explained by the reaction of the sulphuretted ammonium sulphide on the carboxyl-

group, with evolution of hydrogen sulphide and separation of sulphur.

Methyl meta-xylyl ketone under similar conditions yields a compound of the formula $C_{10}H_{13}NO_7$ which crystallises in delicate needles, melting at 183°, soluble in alcohol and ether.

Acetophenone forms a compound of similar composition, but tolyl phenyl ketone yields tolylphenylmethane, and anthraquinone yields anthranol. V. H. V.

Tetrachlorobenzoic Acid and its Derivatives. By P. Tust (*Ber.*, **20**, 2439—2442). — *Tetrachlorobenzoic acid*, $C_6HCl_4{\cdot}COOH$ [$COOH : Cl_4 = 1 : 2 : 3 : 4 : 5$], is readily obtained by heating tetrachlorophthalic acid with glacial acetic acid for 3 to 4 hours at 300°, and crystallising the crude product from water. It forms in colourless needles melting at 186°, sparingly soluble in water, soluble in alcohol and ether. Its *barium* and *calcium* salts are sparingly soluble in water, the *lead* and *copper* salts, insoluble; the *ethyl* salt crystallises in colourless needles melting at 34·5°. An acid of the same melting point has previously been described by Beilstein and Kuhlberg (*Annalen*, **152**, 245). The *nitro-derivative*, $NO_2{\cdot}C_6Cl_4{\cdot}COOH$, crystallises in glistening leaflets, its barium salts with $2\frac{1}{2}H_2O$ in colourless needles, and the calcium salt in leaflets. On reduction, the corresponding *amido-compound* or tetrachloranthranilic acid, $NH_2{\cdot}C_6Cl_4{\cdot}COOH$, is produced, which separates in white insoluble flocks; its alkaline earth and copper salts are also insoluble. V. H. V.

Constitution of Phenyl-α- and Phenyl-α-β-hydroxypropionic Acids. By E. Erlenmeyer, jun. (*Ber.*, **20**, 2465—2466).—The acid described by Plochl as phenylglycidic acid has been shown by the author to be phenylpyruvic acid, as evidenced by its reactions with phenylhydrazine, hydroxylamine, and thiophen (this vol., p. 142). On the other hand, Glaser's phenylhydroxyacrylic acid is probably, as supposed by Erlenmeyer, sen., phenylglycidic or phenyl-α-β-hydroxypropionic acid. In the paper this view is confirmed by the formation from the sodium salt of the acid of phenyl-β-chloro-α-hydroxypropionic acid, identical with that obtained by Leschhorn from phenylglyceric acid. The salts of this acid, when decomposed with aqueous soda, yield a sodium phenylhydroxyacrylate identical with that obtained from phenyl-α-chlorolactic acid. The constitution of Glaser's acid is expressed by the formula $<^{CHPh}_{\quad O\quad}>CH{\cdot}COOH$, whilst Plöchl's acid has the formula $CH_2Ph{\cdot}CO{\cdot}COOH$.

V. H. V.

Action of Aniline on Ethyl Dibromosuccinate. By N. Lopatine (*Compt. rend.*, **105**, 230—231).—10 parts of ethyl dibromosuccinate, 20 parts of aniline, and 40 parts of alcohol of 95 per cent. are boiled together for 12 hours. A precipitate gradually forms and eventually the mass becomes solid. The product is treated with cold

alcohol, and the residue is dissolved in boiling alcohol which, when cooled, deposits silky needles of the composition

$$COOEt{\cdot}CH(NHPh){\cdot}CH(NHPh){\cdot}COOEt.$$

This compound forms long, rhomboidal prisms which melt without decomposition at 145°, and are insoluble in boiling water, and only slightly soluble in alcohol or boiling benzene. When heated with barium hydroxide, it decomposes with evolution of carbonic anhydride; with potash solution, it yields a crystalline substance soluble in water and in alcohol, and it forms a crystalline product with hydrogen chloride. C. H. B.

Glycosuric Acid. By J. Marshall (*Arch. Pharm.* [3], **25**, 593).—This new acid, extracted from pathological urine, reduces Fehling's solution more strongly than does glucose. *Glycosuric acid* crystallises in the form of opaque tetragonal prisms, which melt at 140°, dissolve easily in water, alcohol, and ether, less easily in chloroform, and not at all in benzene, toluene, and light petroleum. To prepare it, the urine is treated with half its volume of lead acetate, the precipitate after being washed with 45 per cent. alcohol, is suspended in warm water and freed from lead by means of hydrogen sulphide. The boiled filtrate after treatment with excess of lead carbonate, is again boiled, filtered, and evaporated to crystallisation. The lead salt thus obtained is washed with 45 per cent. alcohol, dissolved in water, decomposed by hydrogen sulphide, boiled, and the filtrate evaporated to dryness at 70°; the residue extracted with ether is finally allowed to evaporate spontaneously. The crystals thus obtained are still very impure and require repeated crystallisation from ether, ether containing water, and lastly water alone. Glycosuric acid contains neither oxygen nor nitrogen: animal charcoal absorbs it completely; picric acid gives no brown colour reaction, on the contrary aqueous soda solution gives a brown reaction. Bismuth salt in Böttger's test is not reduced; but Fehling's solution and silver nitrate are reduced. Fermentative action was not observed, neither does the aqueous solution affect polarised light. Neutral dilute ferric chloride solution produces a blue colour which soon disappears. The new acid may be considered as a derivative of phenol. A characteristic reaction, similar to that of murexide, may be observed on evaporating at 60° the solution in ether. The solution takes a wine-red colour, which is imparted to the separating crystals; on dissolving the latter in water, however, the colour disappears. J. T.

Behaviour of Aromatic Sulphinic Ethers towards Hydrogen Sulphide. By R. Otto and A. Rössing (*Ber.*, **20**, 2275—2278).—When hydrogen sulphide is passed through ethyl benzenesulphinate heated at 45—50°, ethyl hydrogen sulphide and benzenesulphinic acid are formed. The sulphinic acid can be isolated only partially, as it further decomposes into benzenesulphonic acid and benzene disulphoxide. The greater part of the ethereal salt is, however, converted into phenyl ethyl sulphide with separation of sulphur. Ethyl paratoluenesulphinate

is converted by hydrogen sulphide into paratoluenesulphonic acid (in small amount), tolyl hydrogen sulphide, toluenesulphinic acid, ethyl hydrogen sulphide, sulphur, and a thick oil, probably consisting of toluene polysulphides. No ethyl tolyl sulphide is formed in the reaction. N. H. M.

Manufacture of α-Naphthylamine. By O. N. Witt (*Ding. polyt. J.*, **265**, 225—230).—An important feature in the success attending the manufacture of naphthylamine is the purity of the naphthalene employed. The nitration is effected in cast-iron cylinders fitted with stirrers and cooling jacket. The charge consists of 250 kilos. of naphthalene, 200 kilos. of nitric acid of 40° Baumé, 200 kilos. of sulphuric acid of 66° Baumé, and 600 kilos. of the waste acid from a previous nitration, the latter being used as diluent. The nitration is performed at 45—50°, the temperature being regulated by the rate at which the naphthalene is added and the flow of cold water through the cooling jacket. The reaction is completed in about 12 hours. The contents of the apparatus are then transferred to wooden vats lined with lead and allowed to cool. The waste acid is run off and the nitronaphthalene boiled out with water until free from acid. It is then reduced in apparatus similar in construction to those employed in the manufacture of aniline. For this purpose, 600 kilos. of air-dried nitronaphthalene are added gradually to a mixture of 800 kilos. of iron borings and 40 kilos. of hydrochloric acid, the temperature being regulated by the introduction of the nitro-product, so that it is about 50°. When all the nitronaphthalene has been put in, the operation is continued for 6—8 hours, the temperature being kept at 50°. At the end of the reduction, milk of lime is stirred into the mass, and the contents are transferred to shallow iron trays and distilled in retorts constructed to carry several tiers of trays. The distillation is assisted by the introduction of superheated steam. A black oil is obtained which solidifies on cooling. The crude product is purified by rectification in wrought-iron stills which are heated directly by the fire. Naphthylamine comes over as an almost colourless oil, which is poured into moulds to solidify, when it forms crystalline cakes which are light grey or nearly white.

The author is of opinion that the reduction of nitronaphthalene is effected essentially by ferrous chloride, which during the reaction is converted into a basic chloride, possibly Fe_2Cl_4O, according to the following equation:—$24FeCl_2 + 4C_{10}H_7\cdot NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_{10}H_7\cdot NH_2$. The basic compound is then attacked by the excess of iron, and reduced to ferrous chloride with formation of ferrosoferric oxide, thus: $12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2$. The ferrous chloride then acts on a further portion of nitronaphthalene.

As commercial naphthylamine is frequently supposed to contain small quantities of the beta-compound, the author has made a series of experiments, the results of which showed that no trace of β-naphthylamine is formed. The author has, however, detected the presence of a base in crude naphthylamine, which judging from its properties seems to be *paranaphthylenediamine*. D. B.

Action of Bromine on Anthranol. By F. Goldmann (*Ber.*, **20**, 2436—2437).—When two molecular proportions of bromine are added to one proportion of anthranol dissolved in carbon bisulphide, *anthraquinone dibromide*, $C_6H_4<^{-CO-}_{CBr_2}>C_6H_4$, separates in large, rhombic crystals, decomposed by acetic acid with formation of anthraquinone. If, however, one proportion of bromine is used, *bromanthranol*, $C_6H_4<^{C(OH)}_{-CBr-}>C_6H_4$, is produced, which crystallises in small, transparent tables melting at 148—151°, soluble in carbon bisulphide and chloroform. V. H. V.

Erythrolhydroxyanthraquinonecarboxylic Acid. By W. Birukoff (*Ber.*, **20**, 2438—2439).—Methylerythrohydroxyanthraquinone, when heated with concentrated sulphuric acid, yields a *carboxylic acid* by oxidation of the methyl-group, with evolution of sulphurous anhydride. The acid, $C_{15}H_8O_5$, crystallises in citron-yellow needles melting at 236—238° with decomposition; it is readily soluble in water and ammonia, thus differing from the methyl compound; its *barium* and *calcium salts* are sparingly soluble. When heated above 270°, it is decomposed into carbonic anhydride and erythrohydroxyanthraquinone. V. H. V.

Derivatives of Dianthryl. By A. Gimbel (*Ber.*, **20**, 2433—2435). *Dinitrodianthryl*, $C_{28}H_{16}(NO_2)_2$, obtained by the direct nitration of dianthryl, crystallises in pale-yellow needles melting at 337° with decomposition. When oxidised with chromic acid, it yields anthraquinone, a result which proves that the nitro-groups displace the hydrogen-atoms combined with the central carbon-atoms. On reduction, the nitro-compound is converted into the corresponding *amido*-derivative, $C_{28}H_{16}(NH_2)_2$, which crystallises in glistening, yellow leaflets melting at 307—309° with decomposition. Its *acetyl*-derivative, $C_{28}H_{16}(NHAc)_2$, crystallises in yellow leaflets, sparingly soluble in alcohol and benzene; the *picrate* forms brown leaflets decomposed completely by ammonia into acid and base. V. H. V.

Azines of Chrysoquinone. By C. Liebermann and O. N. Witt (*Ber.*, **20**, 2442—2444).—As an extension of the applicability of the azine-reaction of the diketones, the formation and properties of the azine-derivatives of chrysoquinone are described.

Chrysotoluazine, $C_{25}H_{16}N_2$, prepared from chrysoquinone and orthotoluenediamine, crystallises in yellow, glistening needles; the corresponding *naphthyl*-derivative, $C_{28}H_{16}N_2$, is a yellow, minutely crystalline powder. The formation of these compounds confirms the analogy of chrysoquinone with phenanthraquinone. Picequinone did not yield satisfactory results, but only a large quantity of a tarry matter; in this respect it resembles β-naphthaquinone. V. H. V.

Derivatives of Camphor. By L. Balbiano (*Gazzetta*, **17**, 155—164).—As V. Meyer has recently raised the question as to whether the phenylhydrazine reaction can be considered to be charac-

teristic of ketonic and aldehydic compounds only, the constitution and reactions of camphyldiphenylhydrazine are here discussed. This compound, when decomposed by hydrochloric acid, yields aniline and ammonia in considerable quantities, together with phenylhydrazine and a rather indefinite resinous substance; the latter is considered to be a nitrile as, when boiled with alkali, it yields ammonia and acid compounds, and gives a basic substance, $C_{16}H_{25}N_3$, on hydrogenation. This base forms a hydrochloride melting at 155—157°, and crystallising in delicate needles, very soluble in water. Its solution reduces the salts of the heavy metals and Fehling's solution. The compound is probably a camphylamine in which one of the hydrogen-atoms is displaced by the phenylhydrazine residue. V. H. V.

Racemic Camphol and its Derivatives. By A. Haller (*Compt. rend.*, **105**, 66—68).—The author has prepared and examined camphol, camphor, monobromocamphor, and camphoric acid, inactive by compensation. The last three compounds were obtained in two ways, namely, by mixing dextrogyrate and lævogyrate compounds in equivalent proportions, and by oxidising racemic camphol to camphor, part of which was then used for the preparation of a monobromocamphor, and part for the preparation of camphoric acid. The product of bromination in the latter case is a buttery mass very difficult to purify. No variations in the mode of preparation gave a better product. Similar difficulties have been experienced with other racemic compounds. The melting points of the products are as follows:—

	By mixture.	From camphol.
Racemic camphol.....	210·3°	—
„ camphor	178·6	178·8°
„ monobromcamphor	51·1	51·1
„ camphoric acid.....	204·8	205·2

The melting points of the corresponding optically active compounds are camphol, 208—210°; camphor, 177—178°; monobromcamphor, 76°; camphoric acid, 187°.

The racemic compounds obtained by the two methods are identical, but there is considerable difference between the melting points of the racemic compounds and the corresponding active substances. Their solubilities are likewise different; racemic monobromocamphor is more soluble in alcohol than the active derivative, whilst racemic camphoric acid is less soluble than the active modifications. C. H. B.

Inactive Borneols yielding Active Camphors. By A. Haller (*Compt. rend.*, **105**, 227—230).—The author confirms Montgolfier's earlier results.

Montgolfier has shown that when camphol is heated with sodium, the rotatory power increases. It seemed probable that the camphol obtained by the action of the sodium on camphor is a mixture of equivalent quantities of the dextrogyrate and lævogyrate modifications, but that the sodium acts on the unstable modification, and converts it into the more stable form. This supposition is confirmed by the

following results. 100 grams of camphor was dissolved in 250 grams of toluene, and mixed with 5 grams of sodium (one-third the theoretical quantity). The mixture was heated, and when the action began the lamp was removed. The liquid was then saturated with carbonic anhydride, agitated with water, and the aqueous solution removed and allowed to remain for several days, when the borneol separates out and can be purified by the usual methods. This experiment was repeated with both dextrogyrate and lævogyrate camphors, and the melting points and rotatory powers of the products were as follows:—

	M. p.	Rotatory power. $[\alpha]_D$.
Dextrogyrate camphor	178·4°	+41° 44′
Camphol	210·4	0 0
Camphocarbonic acid.....	128·7	+66 7
Regenerated camphor.....	178·6	+41 44
Lævogyrate camphor	178·6	−42 76
Camphol	210·6	0 0
Camphocarbonic acid	128·7	−66 86
Regenerated camphor.....	178·6	−42 7

It is evident that when camphor is converted into borneol and back, its rotatory power does not alter. It would seem that by whatever process camphor is hydrogenised, the product is never a single substance, but always an unstable mixture. C. H. B.

Alkannin. By C. Liebermann and M. Römer (*Ber.*, **20**, 2428—2431).—Although alkannin, the colouring matter of the alkanna root, was described more than 70 years ago, and has frequently been investigated, yet at present little is known as regards its constitution. Carnelutti and Nasini (Abstr., 1881, 53) ascribe to it a formula $C_{15}H_{44}O_4$, and state that of the hydrogen-atoms two may be displaced by acetyl. As the tinctorial properties of alkannin resemble those of quinalizarin, and their absorption spectra are similar, the authors prepared considerable quantities of the dye; the process used is fully described. The results of analysis pointed to a formula either identical with that of Carnelutti and Nasini or to $C_{15}H_{12}O_4$. When alkannin is passed over hot zinc-dust, methylanthracene is formed (m. p. 175—177°), a result which points to the constitution of alkannin as a derivative of methylanthracene, probably the dihydroquinone or its dihydride. V. H. V.

Ruberythric Acid. By C. Liebermann and O. Bergami (*Ber.*, **20**, 2241—2247).—Ruberythric acid, $C_{26}H_{28}O_{14}$, is obtained by extracting powdered madder root with absolute alcohol (9 litres of alcohol to 1 kilo. of root). The yield was 0·1 per cent. of the weight of root. It is identical with Schunck's rubianic acid, and has all the properties ascribed to it by Rochleder. It forms lemon-coloured needles of a silky lustre, which melt at 258—260°. The *octacetyl-derivative*, $C_{26}H_{20}Ac_8O_6$, crystallises in bright yellow needles melting at 230°; it

dissolves readily in glacial acetic acid, sparingly in alcohol, and is insoluble in water. The acetyl compound was decomposed, and the alizarin, sugar, and acetic acid determined. The following two constitutional formulæ are suggested for ruberythric acid, preference being given to the second:—

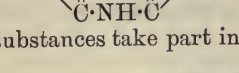
$$C_{14}H_6[O{\cdot}C_6H_7O(OH)_4]_2 \text{ and } OH{\cdot}C_{14}H_6O_2{\cdot}O{\cdot}C_{12}H_{14}O_3(OH)_7.$$

The authors intend preparing the ethyl salt of the acid, which, assuming the correctness of the second formula, should decompose into the acid ether of alizarin and sugar. N. H. M.

Action of Acetone on Pyrroline. By M. Dennstedt and J. Zimmermann (*Ber.*, **20**, 2449—2459).—One of the products of the condensation of acetone with pyrroline by hydrochloric acid (compare this vol., p. 598) is a crystalline substance, to which the authors attribute the formula $C_{14}H_{18}N_2$, as obtained thus:—$2C_3H_6O + 2C_4H_5N = C_{14}H_{18}N_2 + 2H_2O$. To this same compound, Baeyer assigned the formula $C_{14}H_{26}O_2$, and considered that hydrogen was evolved in the course of the reaction, a view not confirmed by investigations described in this paper. The substance crystallises either in pale-yellow or colourless crystals belonging to the tetragonal system: axial ratio $a : c = 1 : 0{\cdot}8343$; observed faces, ∞P, P, 2P, 5P. As regards its constitution, it is pointed out that the imide-group of pyrroline is attacked in the reaction, inasmuch as no acetyl- or potassium-derivative is obtainable; with silver nitrate, it gives a compound which crystallises in needles, and is not a substitution but an additive product, $(C_{14}H_{18}N_2)_2,AgNO_3$.

In like manner, methyl ethyl ketone yields a compound $3C_{16}H_{22}N_2 + 5H_2O$, which forms glistening crystals melting at 142° when anhydrous; so also diethyl ketone yields a compound, $C_{18}H_{26}N_2$, melting at 208—210°. Both substances form crystalline combinations with silver nitrate.

On fractionation of the crude product of the condensation of acetone with pyrroline, an oil is obtained boiling at 275—285°, and of the composition $C_{10}H_{13}N$; this is shown to be a derivative of pyrroline in that it gives the pinewood reaction, and a yellow precipitate with mercuric chloride. Potassium also dissolves in it with evolution of hydrogen. To it is ascribed the following constitutional formula:



CMe_2 (C—C ‖ ‖ C·NH·C) CMe_2; probably several molecules of the reacting substances take part in its formation. V. H. V.

Formation of Pyrrolidine. By A. Ladenburg (*Ber.*, **20**, 2215—2216).—A solution of succinimide in absolute alcohol is warmed on a water-bath and gradually treated with a large excess of sodium. The product is diluted with water and distilled so long as the distillate is alkaline; the latter is made slightly acid, distilled until free from alcohol, and evaporated to a small bulk. The solution is precipitated with bismuth potassium iodide, and the precipitate washed and distilled with soda; the free base thus obtained is then converted into

the platinochloride and crystallised from alcohol. The yield of pure pyrrolidine is small. The author hopes to obtain phenyleneethylenimine from phthalimide by means of this reaction. N. H. M.

Pyridine-derivatives from Metanitrobenzaldehyde. By R. Lepetit (*Ber.*, **20**, 2397—2400).—In a previous communication (this vol., p. 845), the author has described the formation of lutidine-derivatives by the action of ammonia and ethyl acetoacetate on the isomeric nitrobenzaldehydes. In the present paper, further compounds derived from metanitrobenzaldehyde are described.

Ethyl metahydroxyphenyllutidinedicarboxylate,

$$OH\cdot C_6H_4\cdot C_5NMe_2(COOEt)_2,$$

obtained from the corresponding amido-ether (*loc. cit.*) by means of the diazo-reaction, crystallises in white needles, soluble in benzene, and melting at 174°. The same amido-compound yields well-defined colouring matters with amines, phenols, and naphthols. *Ethyl dimethylamidobenzeneazophenyllutidinedicarboxylate*,

$$NMe_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot C_5NMe_2(COOEt)_2,$$

crystallises in flat, red needles, soluble in alcohol, and melting at 167°. *Ethyl β-naphtholazophenyllutidinedicarboxylate*,

$$OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot C_5NMe_2(COOEt)_2,$$

forms small, silky, scarlet needles, soluble in acetic acid, and melting at 152°. *Metamidophenyllutidinedicarboxylic acid*,

$$NH_2\cdot C_6H_4\cdot C_5NMe_2(COOH)_2,$$

obtained by the hydrolysis of its ethereal salt, forms small, white needles, sparingly soluble in alcohol and water, and melting with decomposition at 238°. The salts are soluble. With amines and phenols, the acid forms dyes similar to those obtained from its ethereal salt. On distillation, its calcium salt yields *metamidophenyllutidine*,

$$NH_2\cdot C_6H_4\cdot C_5NH_2Me_2.$$

This is crystalline, dissolves in benzene, and melts at 110°. Its yellow *picrate* forms minute crystals, and its mercurochloride glistening needles decomposing at 160°. By means of the diazo-reaction, it yields *metahydroxyphenyllutidine*, $OH\cdot C_6H_4\cdot C_5NH_2Me_2$, which forms white crystals, soluble in ether and melting at 191°. It is basic in character, and yields well-characterised *platino- and mercuro-chlorides*. Amidophenyllutidine when treated with nitrobenzene, glycerol, and sulphuric acid, yields *lutidyl-quinolyl*, $C_5NH_2Me_2\cdot C_9NH_6$. This base forms colourless, rhombic crystals, melting at 107—109°. Its *hydrochloride*, *nitrate*, and *auro-* and *platino-chlorides* are all crystalline.

L. T. T.

Pyrimidines. By A. Pinner (*Ber.*, **20**, 2361—2365).—Referring to his last paper on this subject (Abstr., 1886, 45), the author states that the formula $C_{11}N_2H_9Br$ there given for a bromo-derivative is incorrect. The correct formula is $C_{11}N_2H_9BrO$, and the compound is *phenylmethylhydroxybromopyrimidine*, $N\leqslant\begin{matrix}CPh:N\\CMe\cdot CBr\end{matrix}\geqslant C\cdot OH$.

A concentrated aqueous solution of dimethylhydroxypyrimidine, when treated with bromine, yields *dimethylhydroxybromopyrimidine hydrobromide*, $N\leqslant\begin{matrix}CMe:N\\CMe\cdot CBr\end{matrix}\geqslant C\cdot OH,HBr$. This crystallises in colourless needles, moderately soluble in water. *Ethylmethylhydroxybromopyrimidine* crystallises in long, colourless needles, sparingly soluble in water and melting at 194—195°. The formation of a *potassium-derivative* (which crystallises in needles with 1 mol. H_2O) shows the continued presence of a hydroxyl-group.

Phenylmethychloropyrimidine, $C_{11}N_2H_9Cl$ (Abstr., 1885, 158), yields with ammonia *phenylmethylamidopyrimidine*, $C_{11}N_2H_9\cdot NH_2$, which crystallises in prisms or scales and melts at 130°. Its *chloride* and *platinochloride* are crystalline.

When phenylmethylhydroxypyrimidine is treated with a mixture of strong sulphuric and nitric acids, it yields a compound which is probably a *nitro-nitroso-derivative*, $C_{11}N_2H_8O(NO_2)\cdot NO$. It crystallises in needles and melts at 238—243°. When reduced with hydriodic acid, it yields *diamidophenylmethylhydroxypyrimidine*, which crystallises in needles and melts with decomposition at 230—240°. It is soluble in soda solution. The *hydrochloride*, *hydriodide*, and *platinochloride* are crystalline. L. T. T.

Derivatives of Pyrazole. By L. Balbiano (*Gazzetta*, **17**, 176—182).—Wislicenus has recently shown that phenylhydrazine and phthalide combine directly to form the hydrazide of a hydroxymethylbenzoic acid. In the present paper, the reaction between phenylhydrazine and compounds of the type of ethylene oxide is studied: epichlorhydrin being selected as a suitable substance. When phenylhydrazine and epichlorhydrin are heated in presence of benzene, to moderate the action, phenylhydrazine hydrochloride at first separates; the crude product is then heated in an oil-bath to 140° to remove the benzene, and the residue is distilled, when a yellow oil passes over. This substance is shown by its reactions to be a *phenylpyrazole*, $C_3H_3PhN_2$; it is insoluble in water, soluble in alcohol and ether, as also in fuming hydrochloric acid. Its *platinochloride* crystallises in yellowish-red prismatic needles, and its *ethiodide*, $C_9H_8N_2EtI$, in small white prisms melting at 116—117°, soluble in water, sparingly soluble in alcohol.

The formation of a phenylpyrazole in the above reaction is explained thus: $C_3H_5OCl + 2PhN_2H_3 = C_3H_5O\cdot N_2H_2Ph + PhN_2H_3,HCl = NH_2Ph + NH_4Cl + H_2O + C_3H_3N_2Ph$.

It would appear from this reaction that in the pyrazole the two atoms of nitrogen are combined to all three atoms of carbon, and thus it differs from the pyrazole obtained by Knorr, in which the nitrogen-atoms are combined with only two carbon-atoms; further investigation is required, however, to settle this point. V. H. V.

Action of Carbamide on Cyanhydrins. By A. Pinner and J. Lifschütz (*Ber.*, **20**, 2351—2358).—When the cyanhydrins of aldehydes are heated with carbamides, derivatives of carbamide of the general formula $CN\cdot CHR\cdot NH\cdot CONH_2$ are formed. Attempts to

obtain the corresponding acids by hydrolysis of these compounds with alkalis yielded only uncertain results, but when the saponification was carried out with dilute acids, anhydrides of the corresponding acids were obtained of the general formula $CO<^{CHR\cdot NH}_{NH\cdot CO}>$. This class of compounds, to which the authors give the name *metapyrazolones*, pass easily into isomeric compounds of the formula $OH\cdot C<^{CHR\cdot N}_{N}>C\cdot OH$ or $OH\cdot C<^{CHR\cdot NH}_{N\cdot CO}>$, to which the authors ascribe the name *metapyrazoles*, as they differ from Knorr's pyrazoles mainly by having the two nitrogen-atoms separated by a CO-group.

Phenylcrotononitrilecarbamide, $CHPh:CH\cdot CH(CN)\cdot NH\cdot CONH_2$, formed from cinnamaldehyde cyanhydrin and carbamide, crystallises in needles easily soluble in boiling alcohol, very sparingly in boiling water. It melts with decomposition at 160°. Alkalis convert it into a mixture of acid compounds. When boiled with dilute hydrochloric acid, it yields *styrylmetapyrazolone*, $CHPh:CH\cdot CH<^{CO\cdot NH}_{NH\cdot CO}>$, which crystallises in glistening, white scales easily soluble in alcohol, sparingly in boiling water. This melts at 171—172°, but if retained at this temperature resolidifies after a time to the isomeric compound *styrylmetapyrazole*, which melts at 194—195°. The same conversion seems to be brought about by dissolving the pyrazolone in boiling water containing a little alkali. The pyrazole obtained by fusion forms small needles which, even after repeated recrystallisation, melt at 194—195°; that by heating with water forms flat needles melting at 190°, but in other respects they are similar, and are both easily soluble in acids and alkalis. The authors cannot at present determine whether these two substances are identical or isomeric.

Phenylacetonitrilecarbamide, $CN\cdot CHPh\cdot NH\cdot CONH_2$, prepared from benzaldehyde cyanhydrin, forms long prisms easily soluble in alcohol and boiling water and melting with decomposition at 170°. With acids, it yields a compound, $C_9H_9N_2O_2$, which crystallises in quadratic scales, is easily soluble in alcohol and boiling water, and melts at 181—182°. Neither heating nor the action of alkalis converts it into an isomeride, and it is therefore probably *phenylmetapyrazole*. It is easily soluble in alkalis and in acids.

Isobutyronitrilecarbamide, $C_4H_9\cdot CH(CN)\cdot NH\cdot CONH_2$, from isovaleraldehyde cyanhydrin and carbamide, is an oil soluble in alcohol and ether, insoluble in water. With hydrochloric acid, it yields *isobutylmetapyrazole*, $C_4H_9\cdot CH<^{C(OH)}_{NH\cdot CO}>N$, which forms small, white needles, soluble in alcohol and boiling water and melting at 209—210°. The isomeric pyrazolone does not appear to be formed. Besides the above oil, a small quantity of imidoisocapronitrile (Erlenmeyer, Abstr., 1882, 191), $NH(C_5H_{10}\cdot CN)_2$, is obtained. Its hydrochloride forms silky needles soluble in alcohol, insoluble in ether.

Similar compounds appear to be obtainable from acetaldehyde cyanhydrin, and are now under investigation. L. T. T.

Sparteïne. By F. Ahrens (*Ber.*, **20**, 2218—2222).—*Dihydrosparteïne*, $C_{15}H_{28}N_2$, is prepared by reducing sparteïne dissolved in strong hydrochloric acid with a slight excess of tin. The hydrochloride obtained by decomposing the stannochloride with hydrogen sulphide is treated with potassium nitrite and the nitroso-compound extracted with benzene; it is then decomposed by hydrochloric acid, the hydrochloride treated with potash and steam-distilled. It is a thick, colourless oil, which boils at 281—284°. The *platinochloride* crystallises well, and becomes black at 239°. The *picrate* forms matted needles which melt at 123—125° and decompose at 215°. The *mercurochloride* crystallises in long needles; the *hydrochloride* and *sulphate* were also prepared.

When sparteïne is added to a solution of hydrogen peroxide, it dissolves with evolution of gas. The product of the reaction is an almost colourless *base*, $C_{15}H_{26}N_2O_2$; this could not be obtained crystalline and distils with difficulty with steam; it dissolves readily in water and alcohol, sparingly in benzene and chloroform, and is insoluble in ether. The *platinochloride*, $C_{15}H_{26}N_2O_2,H_2PtCl_6$, becomes black at 235°; the *aurochloride* crystallises in densely matted needles melting at 143—146°; the aqueous solution decomposes quickly when warmed, with separation of gold. The *sulphate* forms a thick syrup; the *hydriodide* separates from its solution in colourless, feathery crystals melting at 121—122°; the *picrate* and *mercurochloride* were also prepared. N. H. M.

Reactions of Creatinine. By G. Colasanti (*Gazzetta*, **17**, 129—133).—The most delicate test for creatinine in the presence of other reducing agents is that proposed by Weyl, which consists in adding to the liquid to be examined a few drops of sodium nitroprusside and a dilute solution of sodium hydroxide, which gives a yellow coloration. On adding acetic acid and warming an emerald-green colour is produced at first, which changes after some time to blue, a reaction peculiar to creatinine according to Salkowski, and to acetone contained in urine according to Nobel. This reaction is due to the formation of a sodium ferrocyanide derived from the decomposition of the nitroprusside and its subsequent conversion into Prussian blue. In the paper it is shown that other organic and inorganic acids can be substituted for acetic acid, and that the creatinine reaction can be obtained even after ammoniacal fermentation has proceeded for some time. The same reaction is also obtained even after the urine has been preserved for 30 months in sterilised vessels. V. H. V.

Acetylhydrocotarnineacetic Acid. By W. Bowman (*Ber.*, **20**, 2431—2433).—Acetic anhydride combines directly with cotarnine to form *acetylhydrocotarnineacetic acid*, $C_{16}H_{19}NO_6$; this substance crystallises in pale-yellow needles melting at 201°, sparingly soluble in water, soluble in alcohol and benzene. Its *silver* and *mercury* salts are white, the *copper* a blue precipitate; the *ethyl* salt crystallises in delicate needles melting at 113°. The acid is decomposed when boiled with dilute hydrochloric acid, forming a hydrochloride of a compound, $C_{16}H_{17}NO_5$. V. H. V.

Identity of Cadaverine with Pentamethylenediamine. By A. Ladenburg (*Ber.*, **20**, 2216—2217).—When a solution of pentamethylenediamine hydrochloride (1 mol.) is mixed with a solution of mercuric chloride (4 mols.), a mercurochloride with 3 mols. $HgCl_2$ is formed (this vol., p. 126); if a greater excess of mercuric chloride is employed, the compound $C_5H_{14}N_2,2HCl,4HgCl_2$ is obtained. The identity of pentamethylenediamine with cadaverine is therefore established. (Compare also this vol., p. 742.) N. H. M.

Hydrastine and its Derivatives. By M. Freund and W. Will (*Ber.*, **20**, 2400—2406).—This is a continuation of the author's previous work (this vol., p. 383). Hydrastinine when treated with an aqueous solution of potash yields hydrohydrastinine and *hydroxyhydrastinine*, $C_{11}H_{11}NO_3$. The reaction appears to take place according to the equation $2C_{11}H_{11}NO_2 + H_2O = C_{11}H_{13}NO_2 + C_{11}H_{11}NO_3$. Hydroxyhydrastinine is a feeble base, crystallises in needles, melts at 97—98°, and distils above 350°. It is easily soluble in alcohol, chloroform, ethyl acetate, benzene, &c. The *hydrochloride* is crystalline, melts at 138°, and is decomposed into acid and the free base by water and by alcohol. The *platinochloride*, $(C_{11}H_{11}NO_3,HCl)_4,PtCl_4$, forms yellow needles melting at 160°; the *aurochloride*,

$$(C_{11}H_{11}NO_3,HCl)_2,AuCl_3,$$

a reddish-brown mass melting at 100°.

Nitrohydroxyhydrastinine, $C_{11}H_{10}NO_3{\cdot}NO_2$, formed by dissolving the base in dilute nitric acid, yields crystals which are soluble in alcohol and acetic acid, and melt at 271°. It is insoluble in hydrochloric acid, sodium carbonate, or ammonia.

Several fresh salts of hydrohydrastine are described. The *hydrochloride*, $C_{11}H_{13}NO_2,HCl$, forms white crystals melting at 273—274°; the *platinochloride*, $(C_{11}H_{13}NO_2)_2,H_2PtCl_6$, yellow scales melting at 216°, the *dichromate*, $(C_{11}H_{13}NO_2)_2,H_2Cr_2O_7$, red scales which explode at 150°. The hydrobromide previously described melts at 272°. The *hydriodide* melts at 232°, the *ethiodide* crystallises in needles melting at 206—207°. Hydrastinine dichromate has the formula

$$(C_{11}H_{11}NO_2)_2H_2Cr_2O_7,$$

and not that previously given. L. T. T.

Synthesis of Pilocarpine. By Hardy and Calmels (*Compt. rend.*, **105**, 68—71).—The synthesis of pilocarpine was effected by converting β-pyridine-α-lactic acid into pilocarpidine, which was then transformed into pilocarpine by oxidation.

One gram β-pyridine-α-lactic acid was mixed with 100 grams of carbon bisulphide and 10 grams of phosphorus bromide and distilled to dryness. The residue was extracted with water, the solution neutralised with baryta, the excess of baryta removed by means of carbonic anhydride, and the solution evaporated to dryness at a temperature not exceeding 60°. The residue thus obtained was purified by repeated treatment with alcohol, and then mixed with hydrobromic acid and auric chloride, when crimson plates of the normal aurobromide of β-pyridine-α-bromopropionic acid are obtained. The gold is removed by means of hydrogen sulphide, and the free acid is heated in

sealed tubes at 150° for several hours with excess of triethylamine. The product is treated with an aqueous solution of potassium carbonate, and the oily drops of the liberated alkaloïd are dissolved in ether-alcohol, and purified by treatment with animal charcoal. When mixed with auric chloride, it yields the modified aurochloride of pilocarpidine, $AuCl_3,C_{10}H_{14}N_2O_2$, melting at 144°.

In order to convert pilocarpidine into pilocarpine, the extra-pyridic nitrogen of the former must be rendered pentavalent by the addition of a methyl-group, whilst the pyridic nitrogen remains trivalent.

When pilocarpidine is mixed with methyl iodide in alcoholic solution at 60—100°, it combines with 1 mol. of methyl iodide, forming a compound which crystallises with difficulty. If this compound is mixed with auric chloride an oily precipitate is formed and gradually changes to large prismatic needles which melt at 152—153° and have the composition $AuCl_4Me,C_{10}H_{14}N_2O_2$. This compound readily loses methyl chloride when fused, and yields modified pilocarpidine aurochloride, melting at 144°. Pilocarpidine mixed with excess of methyl iodide in concentrated methylic solution, and then with fragments of solid potassium hydroxide, care being taken that the temperature does not rise too high, combines with methyl iodide (1), and methyl hydroxide (2), and if this product is treated with carbonic anhydride, and the liberated alcohol removed, a methiodide is obtained identical with that formed by the action of methyl iodide on pilocarpidine at 60°. The hydroxymethylpilocarpidine obtained by the action of silver oxide on the corresponding methiodide, yields pilocarpidine when boiled with water. These results show that it is difficult if not impossible to remove the methyl hydroxide from position (1), and replace it by methyl hydroxide in position (2).

When, however, pilocarpidine methiodide is oxidised by means of silver permanganate, an unstable group, $MeN^{(1)}\cdot MnO_4$, is formed, and decomposes without affecting the remainder of the molecule. An aqueous solution of pilocarpidine methiodide is mixed with silver permanganate until the greater part of the silver iodide is precipitated. Oxidation takes place immediately, and the liquid contains pilocarpine and formic acid. The alkaloïd is liberated by addition of potassium carbonate, and yields the aurochloride $AuCl_3,C_{11}H_{16}NO_2$, melting at 88°. Synthetical pilocarpidine and pilocarpine yield gummy derivatives similar to those obtained by Harnack and Meyer from the natural products. This phenomenon is confined to the gold compounds, and is purely physical.

The physiological action of synthetical pilocarpine is identical with that of the natural alkaloïd. C. H. B.

Physiological Chemistry.

Relation between Muscular Activity and the Chemical Effect of Respiration. By M. Hanriot and C. Richet (*Compt. rend.*, **105**, 76—79).—The work done consisted of raising a weight of 18 kilos. to a height of 0·5 metre several times, the air expired during the

process being collected and measured. The oxygen absorbed was less than that evolved in the form of carbonic anhydride, and the quantity of carbonic anhydride over that originally existing in the air was equal to 4·5 per cent. of the expired gas. This is the limit towards which the proportion of carbonic anhydride in the expired air tends when work is being done. Correcting for the work done in raising the arms and other bodily movements, it was found that ten lifts or 95 kilogrammetres correspond with the absorption of 0·301 litre of oxygen, the evolution of 0·401 litre of carbonic anhydride, or in round numbers, to do work equivalent to 100 kilogrammetres requires the inhalation of 11 litres of air above the normal volume, the absorption of 0·300 litre of oxygen, and the evolution of 0·400 litre of carbonic anhydride. The ratio between the oxygen absorbed and the carbonic anhydride evolved, shows that the chemical change involved is more complicated than the simple oxidation of glucose or glycerol. Assuming that the energy is provided by the combustion of glucose, the 0·8 gram of carbonic anhydride evolved is equivalent to 0·545 gram of glucose, which corresponds with 2·05 cal. or 860 kilogrammetres. The work actually done was 95 kilogrammetres, and hence the efficiency of the human machine is one-ninth. Taking the oxygen absorbed as the basis of calculation, and assuming that it is all used in the combustion of glucose, it corresponds with a development. of heat equivalent to 645 kilogrammetres, and hence the efficiency in this case is one-seventh. C. H. B.

Heat Developed by the Activity of Muscles. By A. Chauveau and Kaufmann (*Compt. rend.*, **105**, 296—301).—The temperature of the muscles of the jaws of a horse was taken by a thermoelectric method, fine needles being inserted one into the left muscle the other into the right muscle. So long as the muscles remained at rest the scale of the galvanometer remained at rest, but when the muscles were active the galvanometer needle began to oscillate. The enervation of one muscle does not affect the relative temperature whilst in repose, but when in action the temperature of the muscle which performs its functions rises. Cooling by radiation and evaporation is prevented by a casing of cotton-wool. The heat developed is calculated from the weight and temperature of the muscle and the quantity of blood which traverses it. The rise of temperature when the muscle is engaged in mastication is 0·42, but when the muscle makes the same movements without doing any work the rise of temperature is 0·47, or the work done corresponds with a rise of temperature of 0·05°. It is evident that a very considerable amount of heat is developed when a muscle is in operation, but only a small part of this energy (one-seventh or one-eighth) is used up in doing useful work. C. H. B.

Action of Micro-organisms from the Mouth and from Fæces on Food-stuffs. By W. Vignal (*Compt. rend.*, **105**, 311—313).—The 19 organisms isolated from the mouth exert very considerable digestive and fermentative action. Many of them dissolve albumin and fibrin, curdle milk, invert saccharose, ferment glucose,

and saccharify starch. Many of them resist the action of the gastric juice, pancreatic juice and bile.

The fæces contain an enormous number of microbes, including at least 10 species, six of which are also found in the mouth. The other four possess digestive and fermentative powers.

These organisms play a very important part in digestive changes, and there is little doubt that these changes are of a much more complex character than is generally supposed. C. H. B.

Sugar in Urine. By C. Méhu (*J. Pharm.* [5], **16**, 145—149).—The author has frequently proved the presence of small quantities of sugar in the urine of persons passing albuminous urine after a longer or shorter course of milk food. The observations have only been made in the cases of patients whose urine was absolutely free from sugar before the milk treatment was commenced. It is only very rarely that the sugar has amounted to 4 grams per kilo. of urine, usually not more than 2 grams occurs. The urine is acidified slightly and boiled to coagulate albumin, filtered, and treated with $\frac{1}{10}$—$\frac{1}{20}$ its volume of basic lead acetate, filtered, and freed from lead by sodium carbonate. The resulting liquid added to its own volume of recently prepared Fehling's solution is heated for 10 minutes in boiling water; the reduction is very evident if sugar is present. The urine must be recent and non-ammoniacal. Preliminary concentration of the liquid at a moderate temperature to one-third its volume favours the reaction. Instead of Fehling's solution, the author has also used a solution of bismuth prepared as follows:—Bismuth subnitrate, 15·3 grams; tartaric acid, 30 grams; soap lye, 360 grams, or fused sodium hydrate, 80 grams. The soap lye is gradually added to the powdered mixture of the two first substances and the volume is made up to 500 c.c. with hot water. The solution is filtered and can be easily preserved. 1 c.c. is added to 10 c.c. of urine and the mixture heated to boiling, or better still heated in a boiling saturated salt solution. If the mixture does not blacken in about 10 minutes, it is concluded to be free from sugar. This reagent does not blacken in contact with uric acid or pure calcium oxalate. It is more certain than Fehling's solution but somewhat less rapid. It is absolutely necessary that the liquid to be tested should be free from albumin and albuminose, or a black precipitate of bismuth sulphide results. In all cases, it is well to filter the liquid before applying the test. J. T.

Per-ruthenic Acid in Histology. By L. Ranvier (*Compt. rend.*, **105**, 145—147).—Per-ruthenic acid is more readily reduced by animal tissues than is osmic acid, but the action is so energetic that no differences are observed in the behaviour of different kinds of tissues, all becoming equally black. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Microbe of the Indigo Fermentation. By E. Alvarez (*Compt. rend*, **105**, 286—289).—In the fermentation of the indigo plant, the colouring matter forms on the surface of the liquid that is in contact with the air, and the fermenting liquid contains an enormous number of bacilli and micrococci which can be isolated and cultivated by the usual methods. A sterilised solution of the indigo plant will not ferment. The fermentation is due to one bacillus alone and is not produced by any other. It is about 3μ long and $1{\cdot}5\mu$ broad with rounded extremities, and groups of six, eight, or more are frequently arranged end to end in the form of a chain. The bacillus is surrounded by a capsule like the bacilli of pneumonia and rhinoscleroma. It is readily cultivated by the ordinary methods, and when placed in an infusion of the plant, indigo is formed, and the bacilli become stained blue and rapidly multiply. The microbes of pneumonia and rhinoscleroma also determine the fermentation of indigo. Other pathogenic microbes produce no effect. The indigo bacillus is strongly pathogenic. When injected subcutaneously, it produces only local effects, but when injected into the veins or any of the more vascular organs, such as the lungs, of the guinea-pig it rapidly causes death. The principal effects are congestion of the digestive tube and strongly marked lesions of the excretory organs. C. H. B.

Aleurone-grains in the Seed of Myristica Surinamensis. By A. Tschirch (*Arch. Pharm.* [3], **25**, 619—623).—The seeds are peculiar in the extraordinary development of the albumin crystalloïds of the aleurone-grains. Each cell is almost filled with a large crystalloïd of the hexagonal system, either a rhombohedron (R) or a combination of the same with the basal plane (R·OR). Twin forms are rare. These crystalloïds form the matrix of very large aleurone-grains. As a rule, to each crystalloïd is attached a greater or less number of globoïds, each including a needle-shaped crystal of calcium oxalate. Besides the globoïds, the oxalate crystals, and the protein-crystalloids, the aleurone-grains also contain a residue of amorphous substance. To separate these constituents, a section is freed from fat by means of ether, then very dilute aqueous potash dissolves the albumin crystalloïds after washing, acetic acid dissolves the globoïds, and then the calcium oxalate is dissolved in dilute hydrochloric acid. J. T.

Examination of Caucasian Madder Root. By O. Bergami (*Ber.*, **20**, 2247—2251).—The dried powdered root was extracted with boiling absolute alcohol, and the extract reduced to $\frac{1}{3}$ to $\frac{1}{4}$ of its bulk by distillation; a yellowish-brown, crystalline substance separated, consisting of crude glucosides. By further evaporation, crystals of cane-sugar were obtained; the mother-liquor from these were treated with water to precipitate the colouring matter present. The method employed in purifying the glucosides is described. The yield

of pure ruberythric acid is 0·1 per cent. of the weight of root. The amount of cane-sugar is about 3 per cent. The pure colouring matter, which consists of alizarin together with much purpurin, amounts to about 6 per cent. of the weight of root. N. H. M.

Experiments with Ensilage in Holland. By H. Thiel (*Bied. Centr.*, 1887, 445—447).—After allowing the grass to make for a day, it was formed into heaps 10 m. square, the outer portions being higher than the inner, whereby a more even mass is produced, the top was then covered with boards, and weighted with stones to 500 kilos. per square metre.

The composition of the ensilage compared with that of some of the same grass made into hay was as follows:—

	Hay in 100 parts.	Ensilage in 300 parts corresponding with 100 parts hay.
Albumin	12·1	13·5
Fat	2·9	5·7
Carbohydrates and lactic acid	32·7	46·8
Crude fibre	23·7	27·0
Ash	7·3	9·0
Water	21·7	213·9

Six milch cows and six heifers were then fed on the hay and ensilage, in addition to other foods including roots and linseed cake. It was afterwards found that those heifers and cows fed with hay increased in live-weight to a greater extent than those fed on the ensilage, the increase being 104 and 64 per cent. respectively. The yield and quality of milk was, however, best from those cattle fed on ensilage.

The editor of the *Centralblatt* considers that this last fact is due more to the individuality of the cows than to the ensilage.

E. W. P.

Analytical Chemistry.

A Source of Error in Gas Analysis. By W. Hempel (*Ber.*, **20**, 2344).—The author points out that cuprous chloride absorbs gases of the ethylene series, but that when such solutions are further brought in contact with carbonic oxide, varying quantities of the hydrocarbons are again evolved. In analyses in which cuprous chloride is used as an absorbent for carbonic oxide, it is therefore necessary first to remove the heavy hydrocarbons. L. L. T.

A Gas-burette which is Independent of Atmospheric Pressure and Temperature. By W. Hempel (*Ber.*, **20**, 2340—2343).—As in Petterson and Palmquist's apparatus (this vol., p. 999) the influence of atmospheric temperature and pressure is obviated by

connecting the measuring tube with a closed volume of moist air. The eudiometer is connected at the bottom with a movable mercury receiver, and at the upper end terminates in a Greiner-Friedrich slanting-bore three-way tap with two capillary outlet tubes. One of these tubes serves to draw in the gas to be analysed, the other is connected by a rubber joint with a small U-shaped mercury manometer, the other end of which is similarly connected with the air-chamber. The eudiometer and air-tubes are placed side by side in a cylinder of water. L. T. T.

Estimation of Phosphoric Acid. By MALOT (*J. Pharm.* [5], **16**, 157—159).—This communication is supplementary to one which appeared in the July number of *J. Pharm.* on the titration of phosphoric acid by means of uranium nitrate. The green lake formed by uranium oxide with the colouring matter of cochineal being decomposed by dilute acids, not excepting acetic acid, it is necessary to operate with a liquid slightly acidified with acetic acid. Hence, instead of adding 5 c.c. of sodium acetate solution to the assay slightly acidified with nitric acid, it is better after having brought the colour of cochineal to violet by means of ammonia to remove this colour by adding one or two drops of acetic acid. This also produces the best conditions for the precipitation of phosphoric acid by means of uranium acetate. The solution should be kept boiling, especially at the termination of the operation, which is reached when a definite green tint is produced, neither modified by boiling nor by the further addition of uranium salt. Instead of uranium nitrate, it seems preferable to employ the acetate, whose solution better preserves a constancy of composition if care has been taken to boil during a few hours in order to precipitate phosphate, which is always present in commercial acetate. Alcoholic tincture of cochineal serves as well as the solution obtained by boiling in water. The ammonium magnesium phosphate precipitate need not be dissolved off the filter, but may be thrown along with the latter into a 200 c.c. flask for the titration. This precipitate may be impure, either from the presence of citric or molybdic acid. Either of these acids interferes with the accuracy of the assay. It is convenient to dissolve the ammonium phosphomolybdate in concentrated ammonia, and to precipitate with citro-magnesium solution in a liquid strongly ammoniacal, and to wash once at least with strong ammonia, finishing the washing with dilute ammonia to remove the last traces of citric acid. J. T.

Examination of Crude Soda Lyes and Red Liquors. By W. KALMANN and J. SPÜLLER (*Dingl. polyt. J.*, **264**, 456—459).—In examining crude soda liquors, it is the practice to calculate the total consumption of iodine as sodium sulphide, the separate estimation of sodium sulphite and sodium thiosulphate being rarely attempted owing to the want of a rapid and accurate method. The authors recommend a process based on the insolubility of barium sulphite and the solubility of barium thiosulphate in alkaline solutions. The estimation is performed in the following manner:—(1.) The total

alkalinity is determined in a measured volume of the liquor under examination by titration with normal acid, methyl-orange being used as indicator. The acid consumed equals sodium carbonate + sodium sulphide, + sodium hydroxide, + one-half sodium sulphite (Na_2SO_3 is alkaline and $NaHSO_3$ neutral to methyl-orange). (2.) An equal volume of the liquor is titrated with a decinormal solution of iodine, the volume consumed corresponding with the sodium sulphide + the sodium sulphite, + the sodium thiosulphate. (3.) Twice the volume of liquor as that used in (1) and (2) is precipitated with an alkaline zinc solution, and the mixture made up to a certain measure, one-half of which is filtered, acidified, and titrated with decinormal iodine solution. The iodine consumed equals sodium sulphite + sodium thiosulphate. (4.) Three or four times the volume of liquor used in (1) and (2) is treated with an excess of a solution of barium chloride, the mixture made up to a known volume with water, and filtered. (*a*.) One-third or one-fourth (as the case may be) of the filtrate is titrated with normal acid, the amount used corresponding with the sodium hydroxide + the sodium sulphite. (*b*.) A new third or fourth of the filtrate is acidified and titrated with decinormal iodine solution, the iodine consumed being equal to sodium sulphite + sodium thiosulphate. The calculation is made as follows :—

$2 - 4b$	= A c.c. decinormal iodine solution corresponding to	Na_2SO_3.
$2 - 3$	= B c.c. decinormal iodine solution corresponding to	Na_2S.
$4b - (2—3)$	= C c.c. decinormal iodine solution corresponding to	$Na_2S_2O_3$.
$4a - \frac{1}{10}B$	= D c.c. normal acid corresponding to	NaOH.
$1 - (4a + \frac{1}{10}A)$	= E c.c. normal acid corresponding to	Na_2CO_3.

The results of several test analyses are given. D. B.

Estimation of Titanic Acid. By L. Lévy (*J. Pharm.* [5], **16**, 56—61).—Titanic acid is estimated by fusing the material with hydrogen potassium sulphate, extracting with cold water the mixture of titanate and sulphates thus formed, boiling for six hours to precipitate the titanic acid, calcining, and weighing. In presence of alkalis, magnesium, zinc, aluminium, or copper oxides, it is only necessary to fuse with the sulphate as above, dissolve the mass in water acidified with a sufficient quantity of sulphuric acid, neutralise with potash or ammonia, then add 0·5 gram of sulphuric acid to each 100 c.c. of solution, and finally boil for six hours, constantly replacing the water driven off. This method is not applicable in the case of iron sesquioxide. The results are high. J. T.

General and Physical Chemistry.

Oxygen in the Sun. By J. Trowbridge and C. C. Hutchins (*Phil. Mag.* [5], **24**, 302—310).—In these experiments, a powerful alternating current was caused to pass between electrodes of aluminium, and the spectrum, obtained by a grating, photographed on one half of a photographic plate, then, without altering the arrangement of the apparatus, sunlight was admitted, and its spectrum photographed on the other half of the plate. The wave-lengths of the air or sun spectra were tabulated. The authors point out that in order to be certain of the existence of an element in the sun, the coincidence of a large number of the lines of the element in position and grouping with the dark lines of the solar spectrum is necessary, or else a general similarity in the character of the lines; they find no such coincidence for oxygen so far as they have examined (wave-lengths 3749·8—5033·85). They find that the bright lines of Draper's spectrum vanish in their high-dispersion apparatus, and contain numerous dark lines, and, moreover, that there is no general coincidence between the oxygen lines and the bright spaces of the solar spectrum. H. K. T.

Existence of Carbon in the Sun. By J. Trowbridge and C. C. Hutchins (*Phil. Mag.* [5], **24**, 310—313).—The authors find that the solar spectrum near H contains dark lines exactly agreeing with the spaces between the bright lines of the flutings of the carbon spectrum. The carbon spectrum is wanting in the green and blue. This may be due to the effect of vapour in the sun's atmosphere, the lines due to any element being unaltered, obliterated, or reversed, according to the temperature of the vapour through which the light passes. The temperature of the luminous vapour itself may also vary. Further the spectrum from one element may be partially obliterated by the passage of the light through the vapour of another element. The photographic spectrum of carbon can be obliterated in the green and blue by superimposing upon it that of iron, of nickel, and of cerium. The fluted carbon spectrum of the voltaic arc is due to a reversal of the continuous spectrum of the ignited carbon by its own vapour; hence the temperature of the sun's atmosphere where the carbon is volatilised must approximate to that of the voltaic arc.

H. K. T.

Existence of Certain Elements and Discovery of Platinum in the Sun. By C. C. Hutchins and E. L. Holden (*Phil. Mag.* [5], **24**, 325—330).—The spectra of different metals in the voltaic arc are compared with the solar spectrum by means of apparatus already described (see preceding Abstracts). The authors confirm the results of Lockyer for the metals cadmium, bismuth, silver, potassium, and lithium, whilst they find insufficient coincidence for the metals lead, cerium, molybdenum, uranium, and vanadium. Platinum, which has not hitherto been found in the solar spectrum, gives 64 lines between

wave-lengths 4250 and 4950, 16 of which agree with solar lines, whilst seven are doubtful. H. K. T.

Spectrum Analysis. By A. F. Sundell (*Phil. Mag.* [5], **24**, 98—106).—The author examines the spectra of considerable thicknesses of rarefied gases at low temperatures. The gases were contained in glass tubes, viewed end on, the ends of the tubes being coated with tinfoil connected with the conductors of a Holtz machine.

Air first became luminous at a pressure of 10 to 12 mm.; at 8 mm. the light took up peculiar stratifications, which oscillated rapidly. The spectroscope showed a large number of bands, which are tabulated. With pressures less than 0·0003 mm., the luminosity ceased. The author finds that even with a tube which had been frequently exhausted during a period of four months, evidence of air appears shortly after exhaustion. If the discharge is made to take the form of sparks, luminosity ceases at a pressure of 0·004 mm. Hydrogen, oxygen, and nitrogen were also examined. The first was luminous in the highest vacua; oxygen was brightest at 0·2 mm.; nitrogen gave the same spectrum as air. H. K. T.

Radiant Matter Spectroscopy: Examination of the Residual Glow. By W. Crookes (*Proc. Roy. Soc.*, **42**, 111—131).—The author has devised the following modification of Becquerel's phosphoroscope. The phosphorescent substance in an exhausted bulb is excited in the usual way by the spark from the secondary of an induction coil, and is viewed through a rotating disc having 12 symmetrically placed apertures near its margin. A brass cylinder, one end of which is cut into 12 teeth, is fixed upon the axis of the disc, and two springs, one pressing on the continuous part of the cylinder, and the other (adjustable) rubbing over the teeth, serve to complete the circuit through a battery and the primary of the coil. By adjusting the movable spring the spark from the secondary can be made to coincide with the passage of an aperture between the substance under examination and the eye or a spectroscope, or to precede it by a short interval of time, easily calculated when the velocity of the disc is known. By moving the adjustable spring towards or from the bases of the teeth, the relative duration of the makes and breaks can be varied at pleasure. Since the line spectrum of the residual gas in the bulb has no appreciable duration, much lower vacua are necessary for the examination of the residual glow by this method.

When yttria, free from samaria, is thus examined, it is found that all the bands in its phosphorescent spectrum do not appear at the same speed of rotation. As this is gradually increased they come into view in the order Gβ (545), greenish-blue, and Gα (482), deep blue (duration 0·0035 sec.); Gδ (574), citron (0·0032 sec.); Gζ (647), deep red (0·00175 sec.). At an interval of 0·00125 sec. Gδ and Gβ are equally bright, and Gη just visible; and at 0·000875 sec. all are seen of their usual brightness. The author confirms the absence of the citron band from the spectrum of phosphorescent yttric phosphate.

Elsewhere the author has pointed out that 1 per cent. of lime added to a badly phosphorescing substance containing yttrium or samarium

brings out the phosphorescence well. In the former case, it diminishes the sharpness of the line Gδ, but increases its brightness, as well as that of Gα. In the phosphoroscope, lime is observed also to change the *order* in which the yttric lines appear to Gδ, Gα, Gβ, Gη.

The author attributes this action to the long residual phosphorescence of the lime, which induces or assists certain yttric vibrations (Gδ), and is antagonistic to others (Gβ). The influence of baryta and strontia on the phosphorescence of yttria has also been studied, and the author gives the order of appearance and intensities of the lines. The results cannot well be condensed, the action of each alkaline earth not only being fundamentally different, but varying with the relative proportions of the mixtures. An interesting result is obtained on adding strontia to a mixture of yttria and samaria and viewing it in the phosphoroscope with the wheel rotating rapidly. The line Gδ is then completely suppressed, and a spectrum is obtained undistinguishable from that of Marignac's Yα (*Proc. Roy. Soc.*, **40**, 236).

Many earths and oxides, or mixtures of these with lime, have been examined, mostly as sulphates. The results are given in more or less detail.

Arsenious acid, cadmium, copper, lead, and nickel sulphates, tin, tungsten, and uranium, in small quantity with lime, give the phosphorescence of the latter.

Alumina, giving the crimson line, has a very persistent residual glow. In the phosphoroscope, rubies shine with great brilliancy.

Antimony oxide (5 per cent.) with lime phosphoresces white, with a broad space in the yellow. In the phosphoroscope, the glow is green and very strong: the red and orange are obliterated.

Barium (5 per cent.) with lime, bright reddish-orange phosphorescence, with specks of yellow and violet. The spectrum is continuous, faint in the red, strong in the green, and with a broad black band in the orange.

Bismuth (15 per cent.) with lime, bright reddish-orange. The spectrum shows a broad dark band in the red and orange, a black band in the yellow, and great concentration in the green and blue. In the phosphoroscope, red and orange are obliterated.

Calcium sulphate, greenish-blue phosphorescence, without bands or lines. In the phosphoroscope, the colour is green, red and orange being cut off.

Chromium (5 per cent.) with lime, pale-reddish phosphorescence. The phosphoroscope cuts off red and orange.

Diamonds glowing pale-blue have the longest residual glow; next come those glowing yellow. Those phosphorescing red have no residual glow.

Glucina, rich blue; no residual glow.

Lanthanum sulphate, reddish. The spectrum shows a broad orange band with a sharp line—$1/\lambda^2$ 280—superposed. This is identical with the line Gϵ. Lime changes the colour to yellow, bringing out lines of yttrium and samarium, these being present as impurities. Gβ is, however suppressed, together with a portion of the neighbouring spectrum.

Lead sulphate, nearly white. In the phosphoroscope, red and orange are cut off.

Magnesia, pink; 5 per cent. with lime greenish, turning red as the powder heats.

Potassium with lime, bright. Residual glow persistent.

Samarium (see *Phil. Trans.*, 1885, 709).

Scandium as earth or sulphate, very faint blue.

Sodium sulphate gives a greenish tinge to the phosphorescence of calcium sulphate. The sodium line is visible in the spectrum.

Strontia, rich blue with continuous spectrum. In the phosphoroscope, the glow is bright green, the red and blue ends being cut off.

Thorium, as oxide or sulphate, alone or with lime, does not phosphoresce at all, and the tube rapidly becomes non-conducting, the spark passing across the gauge (37 mm. in air) rather than through the tube; in the same vacuum, when yttria takes the place of thoria, a spark of 7 mm. length in air will pass through the tube. This phenomenon is inexplicable; evidently the passage of electricity through the tube depends mainly on the phosphorogenic properties of the earth opposite the poles.

Thulium and erbium together phosphoresce green (*Proc. Roy. Soc.*, **40**, 77). The spectrum shows a faint blue double line, which is intensified by the presence of lime. Some of the yttrium lines are also seen.

Ytterbium when pure gives blue phosphorescence without bands. Some specimens, not quite pure, give bands in the blue which are intensified by the addition of lime, and which the author has carefully measured. Their origin is still uncertain.

The higher fractions of yttria sometimes show a sharp green line ($1/\lambda_2$ 325 approximately). These fractions phosphoresce of a golden-yellow colour, the fractions at the other end phosphorescing yellowish-green. The green line may possibly belong to a new earth.

The phosphorescence of various mixtures of oxides with yttria (usually as sulphates) is then described. Most earths have the effect of destroying, or diminishing the brilliancy of the yttric phosphorescence. Yttria (5 per cent.) with alumina gives a good yttrium spectrum. In the phosphoroscope, the lines Gβ and Gα first appear together, then Gδ. 0·5 per cent. of bismuth with yttria then suppresses the citron line Gδ, thereby rendering visible the samarium double green line and Gβ. With larger proportions of bismuth, the spectrum either is that of yttrium, or is bad. Cerium and didymium tend to deaden the yttrium spectrum. With zinc (95 per cent.), the phosphorescence is yellowish-white and brilliant. In the phosphoroscope, the colour becomes reddish and the line Gβ appears first. Gδ is suppressed. If samarium is present, its spectrum now comes out distinctly.

Zinc sulphide (Sidot's hexagonal blende, *Compt. rend.*, **62**, 999, and **63**, 188) phosphoresces most brilliantly even in a vacuum of several inches. The glow is then green; but as the exhaustion proceeds it becomes blue at the edges of the crystals. At a high exhaustion, the two colours are of equal brightness, but in the phos-

phoroscope the blue is only seen at a high speed. The green glow lasts for an hour or more.

The author then reviews the evidence on which he bases the claims of the bodies $G\alpha$, $G\beta$, &c., to be regarded as separate entities, and the influence of baryta, strontia, and lime is discussed at length in each case. It is remarkable that the spark spectra of old yttrium, and of the higher and lower fractions obtained from it, are perfectly identical, although the phosphorescent spectra and chemical properties of the three are markedly different. Two theories of the true nature of these substances are suggested, namely, the hypothesis of sub-molecules which differ from each other "according to the position they occupy in the yttrium edifice," and the hypothesis that each of them is an independent element. On the latter view, the spark spectrum of yttrium may be supposed to belong to $G\delta$, which is nowhere completely separated during the process of fractionation. A third view is that of de Boisbaudran, who considers that yttrium is an element giving a spark spectrum, but not phosphorescing in a vacuum; and that the phosphorescent spectra are due to impurities; these are two in number, and are provisionally named $Z\alpha$ and $Z\beta$.

Ch. B.

Sharp Line Spectrum of Phosphorescent Alumina. By W. Crookes (*Chem. News*, **56**, 59—62, 72—74).—A rejoinder to Boisbaudran (this vol., pp. 191, 409, 538, 625, 755). The author has proved by direct experiment the possibility of removing very minute proportions of chromium from large quantities of alumina:—1. By boiling the alkaline solution; 2. By passing chlorine through the alkaline solution; 3. By fractional crystallisation of ammonia alum. All these methods were employed in the preparation of the author's "high alumina," in which not the slightest indication of chromium could be detected, nevertheless a sharp line phosphorescent spectrum was obtained, including the red line; hence proving that alumina without chromium can produce it. Next the author shows that chromium in admixture with glucina, magnesia, lime, zinc oxide and other similar substances, and subjected to heating with and without sulphuric acid, and to temperatures varying from cherry-red to full white, did not show any sharp red line. "The general character of the phosphorescence was reddish-orange, the spectrum being almost continuous, with the extreme red and blue ends obliterated." Hence chromium in many solid solvents does not appear to give the sharp red line spectrum. Moreover, Boisbaudran's chromium-gallium red line has a wave-length λ6897 to 6898 ($= \frac{1}{\lambda^2}$ 2102), very far from the alumina red line λ6940 or $\frac{1}{\lambda^2}$ 2076; besides owing to the chemical analogy of aluminium and gallium, it is quite natural to expect a resemblance in their spectra.

In connection with alumina and samaria (Boisbaudran, this vol., p. 1008), it is shown that alum may be obtained quite free from samaria by fractional crystallisation; hence the author's high alumina is free from this impurity. And he finds that the mixed sulphates of

aluminium and samarium heated to redness give the phosphorescent spectrum of the latter modified by the presence of the former, which is explained in this way: a red heat is not sufficient to decompose the sulphates, and samarium sulphate is phosphorescent, whereas aluminium sulphate is not. On the other hand, when the sulphate mixture is heated at a very high temperature, both are decomposed, and the residue of alumina and samaria gives the new sharp line spectrum of alumina, which might be expected, since samaria alone gives practically no phosphorescent spectrum. Maps and detailed descriptions of the spectra are given in the paper. D. A. L.

Sharp Line Spectra of Phosphorescent Yttria and Lanthana. By W. Crookes (*Chem. News*, **56**, 62, 81—82).—Yttria precipitated from the sulphate by ammonia, and heated to redness, does not phosphoresce; but when ignited at a full white heat, it phosphoresces with a clear yellow light, and gives a spectrum containing sharp lines:—from $\frac{1}{\lambda^2}$ 224 to 370 these are numerous and in many cases sharp lines; then follows a clear space, and from $\frac{1}{\lambda^2}$ 409 to 500 some nebulous groups. A specimen of lanthana, treated in a similar manner, phosphoresced of a superficial yellow colour, and gave a very brilliant spectrum. A line at $\frac{1}{\lambda^2}$ 224, groups of bands from 237 to 285, a band at about 330 and 383, and 407. Maps, tables, and descriptions of both the spectra are furnished in the papers. At present no striking results have been obtained by treating in the same manner niobic acid, samaria, ytterbia, and erbia. D. A. L.

Chemical Structure of Oxygen and Hydrogen, and their Dissociation in the Sun's Atmosphere. By A. Günwald (*Phil. Mag.* [5], **24**, 354—367).—Let $[a]$ be the volume of a primary element in a gaseous substance A, and let $[a']$ be the volume which the element occupies when A has combined with another gas, then the wave-lengths of the rays which the element emits in its first combination are to the wave-lengths which it emits in its second combination, as a $[a] : [a']$. Thus, whilst HCl, HBr, and HI give spectra consisting of hydrogen and halogen lines only, H_2O gives a spectrum which may be obtained by multiplying the second hydrogen spectrum by $\frac{1}{2}$. By this means, water lines hitherto unnoticed have been detected. Further the wave-lengths of the hydrogen spectrum can be divided into two groups, (a) and (b), such that (a) $\times \frac{19}{30}$ and (b) $\times \frac{4}{5}$ give lines in the water-spectrum; hence by the preceding reasoning hydrogen consists of two elements, a and b. Let $[a]$ and $[b]$ be the volumes which they occupy in a unit volume of hydrogen, then $[a] + [b] = 1$, moreover $\frac{19}{30}[a] + \frac{4}{5}[b] = \frac{2}{3}$; $\therefore [a] : [b] = 4 : 1$, or hydrogen consists of 4 vols. of the element a combined with 1 vol. of the element b. Spectra are given for the elements a and b. In accordance with the above principle, the wave-lengths of oxygen and hydrogen multiplied by $\frac{2}{3}$ give the water-spectrum. In the same

way, the oxygen spectrum may be split up into sets of lines, which when multiplied by suitable factors give lines in the compound H spectrum and water-spectrum, and from these factors the formula $O = H' [b_4(b_4c_5)_5]$ is obtained, or oxygen is composed of the modified hydrogen H', which radiates the compound line spectrum of hydrogen, of the element *b*, and of a new element *c*. The composition of carbon and nitrogen is also investigated. By a comparison of the *a* and *b* spectra with the chromospheric lines, it is found that hydrogen exists in a dissociated state in the sun's atmosphere, and that the element *b* is identical with helium $D_3 = 5874{\cdot}9$, whilst the extremely light element *a* forms the corona substance $\lambda = 5315{\cdot}9$, and is named by the author *coronium*. H. K. T.

Photochromatic Properties of Silver Chloride. By G. Staats (*Ber.*, **20**, 2322—2323).—When a well-polished plate of silver is dipped into a 5 per cent. solution of iron chloride, it acquires a slate colour. The plate is taken out of the solution after 10 seconds, dried quickly (without heating), and covered with red, emerald, orange, and cornflower-blue glass. In sunshine, the colours appear on the plate after a few minutes; over-exposed plates, especially blue ones, are brownish. The colours dissolve readily in aqueous ammonia. If the plate is heated before exposure, it acquires first a violet and then a red colour, and at the same time partly loses its sensitiveness to yellow and green light. The experiment is suggested as suitable for a lecture experiment. N. H. M.

Modification of the Ferric Chloride Cell. By T. Moore (*Chem. News*, **56**, 64).—Potassium chlorate, hydrochloric acid, and a very small quantity of bromine are recommended in place of bromine alone (Warren, this vol., p. 413), as more economical and equally efficient for the regeneration of the ferric chloride in ferric chloride cells. Cells composed of zinc and carbon immersed in a strong solution of potassium permanganate and ammonium chloride are suggested for use in batteries for electric bells, &c. Exhausted Leclanché cells can be to a great extent revived by pouring a warm, strong, and slightly acid solution of permanganate into the porous cell. D. A. L.

Electrical Conductivity of Hot Gases. By J. Buchanan (*Phil. Mag.* [5], **24**, 297—302).—In these experiments, small pieces of platinum foil are placed vertically and parallel with a flat gas-flame between them, the platinum discs being connected with the binding screws of a condenser charged from a Leclanché battery, and with the quadrants of an electrometer; one pair of quadrants being connected to earth. The flame being in action, the battery was disconnected, and scale-readings taken at equal intervals of time until zero was nearly reached. From these readings the rate of leakage could be found.

Curves are plotted in which the scale-readings of the electrometer are the ordinates, and the times the abscissæ, and equations are obtained. It was found that the rate of leakage was more rapid when the insulated quadrant was negatively charged than when positive. H. K. T.

Electromotive Dilution Constants of Silver and Copper Salts. By J. Miesler (*Monatsh. Chem.*, 8, 193—196).—Moser (Abstr., 1886, 925) has applied the term electromotive dilution constant to the electromotive force of the current between two solutions of single and double concentration. The values of the constants determined by the present series of experiments are given in the following table :—

	Acetate.	Sulphate.	Nitrate.
Copper	2·3	3·6	—
Lead	2·6	—	8·3
Zinc	5·0	—	11·6
Silver	10·7	12·0	16·2

C. S.

Thermochemical Law conjectured by Pebal respecting Non-reversible Electrolytic Actions. By L. Boltzmamm (*Monatsh. Chem.*, 8, 230—236).—The present paper has been constructed from a few data in the papers left by Pebal, and from some suggestions made to Boltzmann a few days before Pebal's death.

If a current is produced through an electrolytic cell by a difference of potential infinitely little different from the electromotive force of polarisation p, an infinitely slow separation of ions takes place. By including a very large resistance in circuit, the process will be reversed and a very feeble current will flow through the cell, whose electromotive force will be infinitely little different from p. In each case, p will be independent of the strength of the current provided it is small. From the second law of thermodynamics, Helmholtz finds that in such a cell no secondary heat will be produced as long as p is independent of the absolute temperature θ. If, on the contrary, p is a function of θ, a quantity of heat measured by—

$$\alpha\theta \mathrm{I}t\frac{dp}{d\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 1,$$

must be supplied to the cell in order to maintain the temperature constant, in the case where the process is reversed. Here the current of strength I traverses the cell for a time t, and α is the thermal equivalent of a unit of work. This result has been tested by the experiments of Czapski, Gokel, and Jahn, and has been found to be correct. In many cases, however, the actions are not reversible. Pebal believes that Helmholtz's result may be extended to non-reversible actions somewhat on the following grounds :—

In the majority of cases to which the second law of thermodynamics is applied, as, for instance, to the theory of the steam-engine, &c., the immediate circumstances are not strictly reversible. Rather they have to be approximated to by an ideal set of conditions, in which every finite difference of temperature and every sudden transformation of energy is avoided. In a similar manner, Helmholtz's result may possibly be made available for all electrolytic actions by replacing sudden transformations of energy by reversible processes.

Taking as an ideal case that of a Grove's gas-battery, the formula 1 will give correctly the amount of heat produced by secondary causes. In the actual circumstances when bubbles of gas rise through the

electrolyte or are condensed on the surface of the electrodes, the amount of heat will be smaller, but the diminution will be a quantity which depends only on the nature of the gas evolved, and the substance of the electrodes. In the ideal case, then, the total amount of heat will be Q_1 where—

$$Q_1 = \alpha I p t + \alpha I \theta \frac{dp}{d\theta},$$

and if Q be the thermal equivalent of the chemical actions in the cell, Pebal's conjecture is that the quantity $Q_1 - Q$ depends only on the nature of the gas evolved and the substance of the electrodes. A table for eight electrolytes shows that $Q_1 - Q$ is fairly constant, but its value is somewhat greater than might be at first expected.

C. S.

Bunsen's Ice Calorimeter. By C. V. Boys (*Phil. Mag.* [5], **24**, 214—217).—In order to counteract the evil effect of ordinary ice in unduly cooling the inner ice of a Bunsen's calorimeter, the author adapts a cover to the calorimeter so as to provide a comparatively non-conducting air space between the bulb and the outer ice, and thus reduce the conduction to a minimum, this space being in the first place filled with ice-cold water, which is afterwards removed. In one case a melting = 4 mm. of the scale per hour with the cover, and of 27 mm. without, was observed. With this arrangement, the tubes of the instrument must be made longer, and a good packing of ice placed above the bulb.

H. K. T.

New Pyrometer. By E. H. Keiser (*Amer. Chem. J.*, **9**, 296—299).—An air bulb made of hard glass or of metal and having a long capillary neck is connected by a narrow bore rubber tube with an inverted burette; this latter is placed in a wider tube containing water, and closed with a cork and stopcock at the bottom. The two halves of the apparatus having acquired the temperature of the room (t), the water is adjusted to the zero mark and the apparatus connected together.

The value of a constant (c) for the apparatus is determined by heating the bulb to 100° C., and noting the increased volume of air (V) in the burette, and using the formula $t' = t + V/c - V/273 + t$. The bulb being then heated to any other temperature (t') this may be calculated by the above formula.

H. B.

Note.—The author makes no correction for the moisture of the measured air, and takes no precautions as to the dryness or moistness of the air in the bulb.

H. B.

Change in Volume during the Formation of Metallic Oxides. By N. N. Beketoff (*Chem. Centr.*, 1887, 449—450).—The author showed previously that the combination of solid and liquid elements is generally accompanied with decrease of volume and development of heat, the latter being nearly proportional to the former. This relation, which is most striking in the case of the haloïd derivatives of the alkali metals, is also observed in the case of other oxides, the formation of which gives rise to development of heat.

	MgO.	CaO.	Li_2O.	Al_2O_3.
Atomic weight of metal ..	24	40	7	27
Sp. gr. of metal	1·75	1·57	0·58	2·5
At. vol. of metal	13·7	25·4	12·0	10·6
At. wt. of oxygen.....	17·5	17·5	17·5	17·5
Sum of vols. of constituents	31·2	42·9	41·5	73·3
Sp. gr. of oxide.....	3·2—3·6	3·2	1·88	3·8—4·0
Mol. vol. of oxide.....	11·7	17·5	16·0	26·0
Decrease of vol. per cent..	62·0	60·0	61·4	64·0

The formation of all four oxides corresponds with the heat of formation, 120 to 140 cal. In the case of PbO, a diminution in volume of 31 per cent. was observed, the heat of formation being 55 Cal. When the heat of formation is known, it is possible to calculate the contraction, and from the latter the molecular weight when this is unknown. N. H. M.

Action of Acids on Zinc containing Lead. By W. Spring and E. Van Aubel (*Ann. Chim. Phys.* [6], **11**, 505—554).—The authors have investigated the action of hydrochloric, hydrobromic, hydriodic, and sulphuric acids on zinc containing 0·6 per cent. of lead, prepared by melting zinc with litharge. The metal was cast into cylinders 17 mm. in diameter, covered with wax in such a way that only one of the basal planes was exposed to the action of the acid. The hydrogen evolved was collected in the apparatus previously used in investigations on the action of acids on marble (*Bull. Soc. Chim.*, **47**, 927), and the volume of the gas was read off at regular intervals.

In all cases, the evolution of hydrogen is not the most rapid at the commencement of the reaction, that is, when the acid is strongest, but the velocity of the reaction increases until it reaches a maximum, and then decreases in such a way that the rate of solution is proportional to the concentration of the acid, and the portion of the curve beyond the maximum is a right line which cuts the axis of the abscissæ at a point corresponding with complete solution. The first part of the reaction, during which the rate of solution increases whilst the concentration of the acid diminishes, is abnormal, and represents a *period of induction.* If the second part of the curve is prolonged backwards, it cuts the axis of the ordinates at a point which gives the initial velocity on the assumption that there is no period of induction.

The theoretical initial velocity as thus determined increases with the volume of the acid used, the surface of zinc exposed remaining constant. Experiments show that the temperature of the zinc rises more rapidly than that of the surrounding liquid, the difference being greater the greater the mass of the liquid. This increase in the temperature of the metal of course increases the rate of solution. If the mass of the zinc varies whilst the exposed surface remains constant, the smaller the mass the higher the rate of solution, the greatest velocity being observed with spheres. This result is due to the fact that the temperature rises more rapidly in the case of the smaller masses. In the case of the more concentrated acids, spheres of zinc

were employed, and this introduces a further complication, since the area of the surface is continually diminishing as the action proceeds, and the ratio of the surface to the mass is likewise changing. The correction required is given by the expression—

$$S_1 = S_n (\sqrt[3]{n})^2.$$

Metallic zinc has no action on boiling solutions of zinc chloride.

The experiments were made at three different temperatures, 15°, 35°, and 55°, with hydrochloric acid of 5, 10, and 15 per cent., the strengths of the other acids being adjusted so that they were equivalent to the hydrochloric acid solutions.

With the three different concentrations of hydrochloric acid, the ratio of the rate of solution to the concentration of the acid is not the same in all three series when the whole period of solution is taken into account; but if the period of induction is eliminated in the manner already indicated, then the rate of solution in all cases is proportional to the concentration of the acid. For the same temperature, the theoretical initial velocities are proportional to the concentration of the acid. The slight variations of the curves from right lines are due to the differences between the temperatures of the zinc and the surrounding liquid. Measurements of the electrical resistance show that if electrical conductivity exerts any influence during the period of induction, it is without any sensible effect during the second part of the reaction. In order to ascertain the influence of electrolysis during the period of induction, zinc was immersed in hydrochloric acid of 15 per cent. at a temperature of 35°, the surface of the zinc being first covered with a thin layer of gold, platinum, lead, or copper. If the period of induction is due to electrolysis, the rate of solution during that period should vary with the electromotive force of the couple on the surface of the zinc. Possibly also, thermo-electric currents may be produced by the difference in temperature between the zinc and the surrounding liquid, or by differences between the temperatures of different parts of the metal itself. Under these conditions, the actual initial velocity is very great, but gradually diminishes until it reaches a minimum, then rises and attains a maximum, and becomes a right line, indicating that the rate of solution is proportional to the concentration of the acid. It is evident from this result that the period of induction is the time during which the acid by slow action produces at the surface of the metal an infinite number of minute galvanic couples by exposing the particles of lead which are disseminated throughout the zinc. The great diminution in the rate of solution is probably due to the fact that the liberated hydrogen removes mechanically the particles of the foreign metal which had been precipitated on the surface of the zinc. The actual velocity at the commencement of the reaction increases in the following order: —copper, gold, platinum, lead; whilst the theoretical initial velocity increases in the order, copper, lead, gold, platinum. Neither of these series follows the order of the electromotive force of the couples produced, and hence it is evident that although electrolytic action plays an important part in the solution of a metal in an acid, it is by no means the only determining cause.

No sensible variations in the rate of solution were observed when considerable quantities of sodium or potassium nitrate or sulphates were added to the liquid, and it would therefore seem that the velocity of the reaction is not greatly affected by the internal friction of the solution.

The influence of temperature is shown by a curve the ordinates of which are the initial velocities whilst the abscissæ are the temperatures. These curves seem to be asymptotic to the axis of the temperatures, and the three curves for the three different degrees of concentration of the acid converge at a point which corresponds with a temperature of $-60°$ to $-70°$. This result seems to indicate that at a temperature below $-70°$ hydrochloric acid will have no action on zinc whatever the concentration of the acid, and it is of interest to recall the well-known fact that liquid hydrogen chloride, which liquefies at about $-70°$, has no action on this metal.

According to Kohlrausch, the maximum conductivity of hydrochloric acid corresponds with a strength of 21 per cent. Acid of 25, 30, or 34 per cent., however, dissolves zinc more quickly than acid of 21 per cent., and from this and the previous results it is evident that the conclusion of De la Rive and of Kajander, that the rate of solution is intimately connected with the electrical conductivity of the acid, is not confirmed.

With hydrobromic acid, the rate of solution is much higher than with hydrochloric acid of corresponding concentration. Under ordinary conditions the curve is not a right line at any phase of the reaction, a result due to the fact that with an increased rate of solution the difference between the temperature of the liquid and that of the metal is much greater, and the perturbations due to this cause are greatly increased. If the conditions are such that the temperature of the zinc is kept constant, it is found that the period of induction is very short, the velocity of solution rapidly attains a maximum, and then decreases with the concentration of the solution, the latter part of the curve being a right line. It is a general result that the period of induction is shorter the greater the concentration of the acid. With hydrochloric acid of 30 per cent., for example, there is practically no period of induction, and the maximum velocity is attained at once. The theoretical initial velocity with hydrobromic acid is 2·29 times that with hydrochloric acid.

With hydriodic acid, the velocity during the period of induction is less than in the case of hydrochloric acid, and the difference is greater the weaker the acids, but after the maximum velocity is attained the rate of solution is the same for both acids, and if the curves are drawn on a small scale they coincide. It follows, of course, that the theoretical initial velocities are practically the same for both acids.

The results with the three haloïd acids are quite different from those obtained in the case of the action of the same acids on marble (*loc. cit.*), in which case the rate of solution is the same for all three. The velocity of the reaction with zinc has no simple relation to the electrical conductivity of the acids, their heats of neutralisation, or the solubilities of the salts produced.

With sulphuric acid, the action is very slow, and the rate of solu-

tion could not be measured with an acid corresponding with 10 per cent. hydrochloric acid. The period of induction lasts for several hours, and hence the metal was always previously covered with a film of precipitated lead. At 36°, the velocity is only one twenty-seventh of that observed in the case of hydrochloric acid. It is possible that the reaction is not of the same kind as with the haloïd acids. It may be that the formation of zinc sulphate in this way is almost entirely a phenomenon of electrolysis, and that the chemical attraction of the acid for the metal is not the determining cause as with the haloïd acids. In the latter case, there is simple substitution of the metal for the hydrogen of the acid, whilst the formation of zinc sulphate may be the result of a series of reactions, such as $Zn + H_2SO_4 = ZnO + H_2 + SO_3$; $SO_3 + H_2O + Aq = H_2SO_4 + Aq$; $ZnO + H_2SO_4 = ZnSO_4 + H_2O$.

Pure zinc, rubbed on the surface with metallic lead, does not dissolve in acids with a velocity similar to that of zinc alloyed with lead, or zinc covered with lead by precipitation. The black residue left on solution of the zinc containing lead is pure lead. The difference in the electromotive force in these cases may be due to the state of division of the lead, or possibly the black substance is an allotropic modification of the lead. If pure zinc is rubbed with this lead-black by means of a spatula, it becomes more soluble in acids. Mercury amalgamates and dissolves the lead-black, and this is probably the reason why amalgamated zinc is not soluble in acids. d'Almeida's view that amalgamated zinc is as soluble as ordinary zinc, but has the property of condensing on its surface a layer of hydrogen which protects it from the acid, is not supported by any evidence.

C. H. B.

Note by Abstractor.—L'Hote has recently shown that perfectly pure zinc does not decompose water, and is not soluble in acids (Abstr., 1886, 204). According to Osmond and Werth (this vol., p. 894), impure zinc when dissolved in acids leaves graphitoidal residues of complicated composition. In one case the composition of the residue agreed with the formula Pb_2Zn. C. H. B.

Integral Weights in Chemistry. By T. S. Hunt (*Phil. Mag.* [5], **24**, 318—324).—The specific gravity of a gaseous body, as compared with hydrogen at normal temperature and pressure, is termed its integral weight. In the same way, the integral weights of liquid and solid substances are represented by the specific gravities of these substances as compared with hydrogen at normal pressure, and at the temperatures at which they are generated from the gaseous or liquid states respectively. Thus the density of water at 100° is 0·95878, hence 1628 vols. of steam at 100° condense to 1 vol. of water at 100°; this value multiplied by 17·9633, gives 29244 as the integral weight of water. From this value, the integral weights of other substances are determined, their specific gravities at their changing point being taken, as compared with water at 100°. The specific gravities so obtained would not deviate much from those obtained at 4°. The coefficient of condensation is obtained by dividing the integral weight of the more complex body by that of the simpler one from which it is derived.

H. K. T.

Inorganic Chemistry.

Combustion of Weighed Amounts of Hydrogen; Atomic Weight of Oxygen. By E. H. Keiser (*Ber.*, **20**, 2323—2325).—Palladium was weighed with and without occluded hydrogen, it was then heated, and the hydrogen thus expelled passed over heated copper oxide. The water which was formed was also weighed. 1·5935 grams of hydrogen (from three experiments) gave 14·23972 grams of water. The atomic weight of oxygen calculated from these numbers is 15·872. The number obtained from Stas's figures is 15·84 (Ostwald, *Allgem. Chem.*, **1**, 43). The author intends repeating the experiments with large amounts of palladium. N. H. M.

Composition of Generator-gas and Water-gas. By F. Fischer (*Ber.*, **20**, 2551—2553).—The following results are given:—

	Generator-gas from		Water-gas from Essen.
	Coal.	Wood.	
CO_2	5·06	6·95	2·71
CO	21·58	28·60	43·75
CH_4	2·91	2·20	0·31
H	5·66	8·54	49·17
N	64·79	53·71	4·06
	100·00	100·00	100·00

The analyses were made in a special apparatus, which, however, presents no very novel features. W. P. W.

Tellurium Dichloride. By A. Michaelis (*Ber.*, **20**, 2488—2492).—Tellurium dichloride melts at about 175°, and boils constantly at 324°. The vapour-density was determined in an atmosphere of nitrogen at the temperature of boiling sulphur, and the following values were obtained: 6·9, 6·6, 7·0, compared with 6·89, the value calculated for $TeCl_2$; moreover, there is no indication that the vapour has a greater density at lower temperatures. The vapour of the dichloride is dull red in colour, and gives a characteristic absorption-spectrum (Gernez, this Journal, 1872, 665), in which the bands, whose positions on an arbitrary scale are given, lie between Fraunhofer's lines *b* and C. When heated in an open tube, the vapour of the dichloride becomes brighter in colour, and finally assumes a pure yellow. This change in colour is accompanied by the disappearance of the absorption-bands, and is due to the oxidation of the dichloride when heated in air, since the compound when heated in a current of oxygen is converted into a mixture of tellurium tetrachloride and tellurium dioxide, together

with the oxychloride $TeOCl_2$, if the heating is continued for some time. The vapour of the tetrachloride is yellow, and gives no absorption-spectrum, a fact which confirms the point brought out in the vapour-density determinations (this vol., p. 770), that the compound is stable, and does not decompose into chlorine and the dichloride when vaporised. W. P. W.

Working-up of Stassfurt Potash Liquors containing a Large Excess of Sodium Chloride. By H. Fischer (*J. pr. Chem.* [2], **36**, 222—224).—Boiling water dissolves much more potassium chloride and sulphate but hardly any more sodium chloride than cold water. Potassium sulphate and potassium magnesium sulphate are less soluble in cold water than potassium and sodium chlorides; and finally the presence of magnesium chloride reduces the solubility of all the above salts except potassium chloride.

Advantage is taken of these relationships to isolate potassium chloride from saline solutions containing but little of this substance. End-liquors (rich in magnesium chloride) are added until the solution contains about a quarter as much magnesium chloride as sodium chloride, and the whole is then concentrated. Sodium chloride separates out first, and then potassium sulphate and potassium magnesium sulphate, potassium chloride remaining dissolved. L. T. T.

Crystalline Form of Potassium Aurobromide. By P. Schottländer (*Annalen*, **240**, 346—348).—Potassium aurobromide crystallises in the monoclinic system.

$$a : b : c = 0{\cdot}79688 : 1 : 0{\cdot}3610 \qquad \beta = 85° 34' 2''.$$

W. C. W.

Analysis and Properties of Phosphorised Silver. By H. N. Warren (*Chem. News*, **56**, 113).—When phosphorus is added to molten silver, the metal on cooling ejects the phosphorus; it however retains sufficient to give the silver a yellow colour, and to prevent it from spitting. The amount retained seldom exceeds 0·002 per cent. of phosphorus, but this is exceedingly difficult to expel by cupellation. D. A. L.

v. d. Pfordten's Silver Suboxide. By C. Friedheim (*Ber.*, **20**, 2554—2557).—The composition of the so-called silver suboxide prepared by v. d. Pfordten (this vol., p. 699) was determined by titration with permanganate, which is stated in the paper to be without action on metallic silver. The author, however, finds that when very finely divided ("molecular") silver suspended in water acidified with dilute sulphuric acid (1 : 5) is titrated with permanganate, the colour disappears as in oxalic acid titrations, slowly at first, then more quickly, and silver goes quantitatively into solution. Experiments made simultaneously with similar quantities of materials show that solution of the metal does not occur in the mixture of silver and sulphuric acid, and that the permanganate is not decolorised when added to the sulphuric acid. Moreover, compact silver is also attacked by permanganate acidified with dilute sulphuric acid; thus in an experiment with 1·5 grams of silver foil, 1 gram was dissolved when shaken for

two hours with the acidified permanganate, and brown flocks of what seems to be a compound of silver oxide with a higher oxidation product of manganese were simultaneously formed.

Following v. d. Pfordten's directions in every particular, a substance was prepared which, to judge from the published description, was identical with the so-called silver suboxide. On titration with permanganate, however, the ratio Ag : O = 2 : 1 was obtained, and further, the volume of the gas not absorbed by aqueous soda which was given off when the substance, after careful drying in an atmosphere of carbonic anhydride, was slowly heated to bright redness was so small that the preparation must have been silver in an almost pure state; moreover, on dissolving the ignited silver in an acid, a residue of carbon was left. These facts lead the author to the conclusion that v. d. Pfordten's silver suboxide is nothing more than finely divided silver rendered impure by the presence of more or less silver oxide or organic substances. W. P. W.

Basic Zinc and Cadmium Nitrates. By H. L. Wells (*Amer. Chem. J.*, **9**, 304—308).—By treating zinc or cadmium nitrate in hot solution with the oxides, and allowing it to cool, crystals of the basic salts, $2ZnO,N_2O_5,3H_2O$ or $2CdO,N_2O_5,3H_2O$, separate, the first in thin scales, the second in needles. Both are decomposed by washing with water, and must therefore be purified by washing with absolute alcohol. The basic salts previously described have been prepared by heating the normal nitrates, or by treating them with ammonia; none of these were washed with alcohol. H. B.

Basic Lead Nitrates. By A. J. Wakeman and H. L. Wells (*Amer. Chem. J.*, **9**, 299—303).—Besides the basic lead nitrate $NO_3{\cdot}Pb{\cdot}OH$, the following salts have been described:—

$6PbO,2N_2O_5,3H_2O$, Berzelius and Meissner; $6PbO,2N_2O_5,H_2O$, Meissner, Löwe, and Smolka; $6PbO,2N_2O_5,2H_2O$, Löwe;

$$6PbO,2N_2O_5,6H_2O,$$

Volge; $10PbO,3N_2O_5,5H_2O$, Smolka and Morawski.

The first salt is prepared without difficulty, but the others prove to be incapable of recrystallisation, or to be mixtures, or to have been imperfectly analysed, the only other recrystallisable basic salt being $10PbO,3N_2O_5,4H_2O$. This substance forms flat, tabular crystals of triclinic habit, with an extinction angle of 35°; it is less soluble than the diplumbic nitrate, and suffers no change by boiling with water or on recrystallisation. All the preparations were examined microscopically, and all mixtures rejected. H. B.

Relations of Mercury to other Metals. By A. C. Cousins (*Chem. News*, **56**, 113—114).—Attention is drawn to the following coincidences:—The atomic weight of mercury is the mean of the atomic weights of gold and thallium. Its sp. gr. in the liquid state is very nearly the mean of their atomic volumes. Its atomic volume is almost the theoretical sp. gr. of an alloy of equal weights of gold and thallium. D. A. L.

Gallium. By L. de Boisbaudran (*Ann. Chim. Phys.* [6], **11**, 429—430).—Gallium chloride twice evaporated to dryness and dried at 100° loses by volatilisation about 0·6 per cent. of gallium. The amount of volatilisation from a hydrochloric acid solution of gallium chloride heated gradually to redness in presence of sulphuric acid, cannot be recognised with 0·08 gram of the chloride. C. H. B.

Metallic Manganese. By T. T. P. B. Warren (*Chem. News*, **56**, 27).—The author found that a sample of manganese he examined was either non-magnetic or only very slightly magnetic. It contained a small quantity of petroleum, which probably affected its magnetic properties. D. A. L.

Compound of Manganese Sesquioxide with Cupric Oxide. By E. A. Schneider (*Amer. Chem. J.*, **9**, 269—274).—Although many compounds of sesquioxides and protoxides are known, none have been prepared in which manganese sesquioxide plays the part of an acid oxide, and only two have been prepared in which copper oxide plays the part of a basic oxide, namely the compounds $CuO,Fe_2O_3 + 5H_2O$ and CuO,Cr_2O_3, and none in which silver oxide or mercuric oxide act in a similar manner.

An ammoniacal cupric oxide solution is mixed with aqueous soda, and to the deep blue solution aqueous manganous chloride is added, best drop by drop, with constant stirring. If the copper oxide and manganic oxides are used in the molecular ratio 1 : 1 or 2 : 1, the whole of the copper is at once removed, but with the ratios 3 : 1 or 4 : 1 or 5 : 1 a portion of the copper remains in solution. The black precipitate thrown down in each case seems to have the composition $Mn_2O_3,3CuO$, although when an excess of copper solution is not used the precipitate approximates more towards $Mn_2O_3,2CuO$. The oxidation is effected by atmospheric air. H. B.

Peculiar Formation in Nickel Regulus. By T. Moore (*Chem. News*, **56**, 3).—On allowing a molten nickel regulus to cool slowly, brilliant flakes separated out, of a symmetrical form, and very ductile and malleable. These flakes had the following composition:—(*a*.) Cu, 160; Ni, 70·30; Fe, 28·30. (*b*.) Cu, 0·25; Ni, 87·863; Fe, 11·865 per cent. Regulus (*a*) contained 13·5 per cent. Fe; (*b*), 15·6. By the exclusion of copper, flakes were obtained composed of 86·40 per cent. Ni with 13·72 Fe, the surrounding regulus containing Ni, 72·10; Fe, 2·32; S, 25·51; whilst the regulus cooled suddenly to prevent formation of flakes had per cent., Ni, 73·80; Fe, 4·27; S, 22·01. It is curious to note the formation of such an alloy, and especially a malleable alloy, in the presence of sulphur. Under favourable conditions, the regulus may contain 10 per cent. of this alloy.

D. A. L.

Germanium. By C. Winkler (*J. pr. Chem.* [2], **36**, 177—209).—In the present communication, the author details the further progress of his researches (Abstr., 1886, 985) on germanium. The investigation of this element is rendered difficult, as the argyrodite vein in the Himmelsfurt Mine is exhausted, and the quantity of

argyrodite in hand is small; this mineral is mainly found as a thin coating over other silver ore, the percentage of germanium in some of the richest ores being only about 0·03 per cent. Slight variations in the mode of extracting the element from the ore from those previously given (*loc. cit.*) are described. The sparing solubility of potassium germaniofluoride may also be employed for this purpose. Powdered argyrodite is mixed with nitre and potassium carbonate, and the mixture introduced in small quantities into a red-hot Hessian crucible. On cooling, two layers are obtained, the lower of silver, the upper of alkali salts. The upper layer, containing all the germanium, is powdered, boiled in water, and the filtered solution treated with excess of sulphuric acid and evaporated to dryness. This acid residue is then dissolved in cold water, when almost all the germanium oxide is gradually deposited from the solution. The remaining germanium is precipitated by hydrogen sulphide, and the sulphide converted into oxide by treatment with nitric acid. The oxides are mixed, dissolved in aqueous hydrofluoric acid, and filtered if necessary; potassium fluoride is added, and the double fluoride separates out. This fluoride is then converted into soluble thio-salt by fusion with potassium carbonate and sulphur, or by digestion with ammonium sulphide, this is decomposed by sulphuric acid, and the germanium precipitated as sulphide with hydrogen sulphide. This sulphide, when mixed with a little sulphuric acid and gently heated, yields a mixture of sulphide and oxide, which is converted into oxide by roasting and treatment with nitric acid. The oxide may be reduced by hydrogen, but if at all in large quantity the following method is preferable:—The powdered oxide is mixed with about 15 to 20 per cent. of starch, and kneaded with a little boiling water into small balls, which are dried at a low heat. These are introduced into crucibles between layers of powdered charcoal, and the whole kept at a bright red heat for about an hour. In this way, a somewhat porous regulus of germanium is obtained, which may be fused with powdered borax glass, and so obtained as a brittle, metallic bead.

When germanium is gently heated in a current of hydrogen chloride, the metal becomes red-hot, hydrogen is evolved, and two liquids of almost identical specific gravity are formed. After some time these separate into two layers. The heavier is the colourless, thin liquid boiling at 72°, previously described (*loc. cit.*) as possibly germanious chloride. Analysis, however, showed it to be *germanium chloroform*, $GeHCl_3$. It is very easily oxidised in contact with air, apparently yielding the oxychloride, and at a high temperature seems to break up according to the equation $2GeHCl_3 = Ge + GeCl_4 + 2HCl$. A vapour-density determination made by Victor Meyer's method at 178° gave 5·55, theory requiring 6·21. The second liquid is *germanium oxychloride*, $GeOCl_2$ (?). It is a colourless, non-fuming, oily liquid, which adheres strongly to glass. It boils much above 100°, seemingly without decomposition, but has not yet been obtained quite pure. The author hopes to obtain germanious chloride by heating germanious sulphide in an atmosphere of hydrochloric acid. Germanic chloride (*loc. cit.*) may be obtained by heating a mixture of germanic sulphide and mercuric chloride. It remains liquid at −100°. *Germanic bromide*,

$GeBr_4$, may be prepared either by heating germanium in bromine vapour, or by heating the powdered metal with mercuric bromide. It is a strongly fuming, colourless liquid, which solidifies a little below 0° to a white, crystalline mass. When poured into water, heat is evolved and germanium oxide precipitated.

Germanious oxide dissolves in strong, aqueous hydrofluoric acid to a clear solution; this, on evaporation over sulphuric acid, yields *germanic fluoride*, GeF_4, as a colourless liquid, which gradually solidifies to a crystalline mass of the formula $GeF_4 + 3H_2O$. It is very deliquescent, and cannot be kept in glass vessels, as it attacks their surfaces. It melts readily in its water of crystallisation, but when more strongly heated hydrogen fluoride and moisture are evolved, and a pellicle of oxide forms. If it is heated to redness, much germanic fluoride is volatilised, about half of the germanium present being left as oxide. Pure anhydrous germanic fluoride has not yet been obtained, but the behaviour of its hydrated compound leaves little doubt that it is a solid, but is also volatilisable. Further experiments as to the action of (1) hydrogen on heated potassium germanium fluoride; (2) of hydrated germanic fluoride heated in a current of carbonic anhydride; (3) of a mixture of germanium oxide, calcium fluoride, and sulphuric acid when heated; and (4) of heat on a mixture of sulphuric acid and potassium germaniofluoride, all point to the same conclusion. The opposite results obtained by Krüss and Wilson (this vol., p. 704) are probably due to the smallness of the quantities of fluoride with which they experimented, being especially favourable to the decomposition into oxide. When the vapours of germanic fluoride are passed into water, a solution of germanic oxide (or acid) and of *hydrofluogermanic acid*, H_2GeF_6, is formed; the latter appears to be volatile at ordinary temperatures, but its boiling point seems to lie slightly above that of water. The acid has not, however, yet been obtained in the pure state. The potassium salt has already been described by Krüss and Nilson. It is best obtained by treating a solution of the oxide in hydrofluoric acid with potassium chloride. One part of this salt requires about 180 parts of water at 18°, or about 36 at 100°, for its solution. The salt stands a dull red heat without change, but melts at a bright red heat, and at a still higher temperature loses weight considerably. These results differ from those obtained by Krüss and Nilson (*loc. cit.*).

Germanic ethide, $GeEt_4$, was prepared by mixing together zinc ethide and germanic chloride. The reaction took place with violence, and cooling was necessary. This compound forms a colourless liquid of slightly alliaceous odour. It is very slightly lighter than water, with which it is not miscible; it boils at 160°, but is slowly volatile even at ordinary temperatures. Germanic ethide is not affected by oxygen at ordinary temperatures, but inflames easily, and then burns with a yellowish-red flame and formation of white fumes of oxide. Its vapour-density, as determined in Victor Meyer's apparatus, is 8·50, theory requiring 6·51. The author is unable to explain the discrepancy. No hydrogen-derivative of germanium has yet been obtained.

Germanium appears to be capable of replacing silicon in ultra-

marine. If a mixture of soda and sulphur is heated in a crucible used for roasting germanium sulphide, a blue colour is produced, but the author has not yet succeeded in obtaining a true germanium ultramarine.

The above results agree very closely with the properties predicted by Mendelejeff for ekasilicon, especially those for the ethide, for which he predicted a sp. gr. of 0·96 and boiling point of 160°. L. T. T.

Separation of Gold from the Platinum Metals. By W. Bettel (*Chem. News*, **56**, 133—134). The author severely criticises Hoffmann and Krüss's paper on this subject. With regard to the sulphurous acid method, it answers well but, on account of the sulphuric acid produced, only for moderate quantities of gold. The results are affected by dilution, temperature, and especially acidity; if too acid, the gold is not completely precipitated, if too neutral traces of platinum come down, but at the proper stage all the gold present is precipitated of a purity of 999·9 to 1000. It is, however, customary to remove platinum as double chloride, and estimate gold in the solution. It is noted that tests made with solutions of gold and platinum are not of much practical use, since the commercial alloys as a rule contain many other substances besides gold and platinum. The author finds the oxalic acid method excellent, and has also used formic acid and formates with success. Hoffmann and Krüss neglected to neutralise the gold solution, and did not provide against loss by the evolution of carbonic anhydride; consequently they obtained low results with the oxalic acid method. These two experimenters, moreover, found that gold precipitated by ferrous chloride was platiniferous, a statement characterised by the author as grossly misleading and inaccurate; he moreover, from considerable experience, confidently affirms the contrary to be the case. D. A. L.

Mineralogical Chemistry.

Antimonite from Valdagno. By E. Luzzatto (*Zeit. Kryst. Min.*, **13**, 303—304).—The antimonite from S. Quirico, near Valdagno, occurs in fibrous, laminated masses between quartz and dolomite. It is associated with kermesite, volgerite, and cervantite (?), products of its alteration. Analysis gave the following results:—

S.	Sb.	Pb.	Fe.	Total.
27·63	69·61	1·84	0·30	99·38

B. H. B.

Tellurium-silver-bismuth from Jalisco, Mexico. By C. F. de Landero (*Zeit. Kryst. Min.*, **13**, 320).—The author deals with the ore introduced by A. del Castillo as tapalpite and described by Rammelsberg as tellurium-bismuth-silver, from the mines of the Sierra de Tapalpa, Jalisco, Mexico. At the San Antonio mines, the

mineral occurs in association with quartz grains and iron pyrites crystals, cemented together by talc. No crystals were observed, the ore forming irregular, finely granular masses with a splintery fracture. It is of a silver-white to steel-grey colour. On fresh fractures, a brilliant, metallic lustre is exhibited. The hardness of the ore is from 2 to 3, and its specific gravity 7·395. Qualitative analysis gave bismuth, silver, sulphur, and tellurium. B. H. B.

Minerals from the Stassfurt Salt Mines. By O. Luedeke (*Zeit. Kryst. Min.*, **13**, 289—293).—*Picromerite.* This mineral was first discovered in 1855 by Scacchi at Vesuvius. It has subsequently been found in the Ascherleben and Leopoldshall salt mines near Stassfurt. In chemical composition, it corresponds with the formula $MgSO_4,K_2SO_4 + 6H_2O$. It crystallises in the monoclinic system, the axial ratio being $a : b : c = 0·7425 : 1 : 0·4965$; $\beta = 74° 52'$.

Bloedite.—Crystals of bloedite have recently been discovered at the von der Heydt and Leopoldshall mines. Analysis of this mineral from the latter locality gave :—

$MgSO_4$.	Na_2SO_4.	H_2O.
36·13	42·90	21·07

These results correspond with the formula $MgSO_4,Na_2SO_4 + 4H_2O$. The author also gives descriptions of crystals of rock salt, of kainite, and of pinnoite (Abstr., 1884, 1271; 1885, 1117) from the Stassfurt mines. B. H. B.

Ignatieffite, a New Variety of Aluminite. By K. K. Flug (*Zeit. Kryst. Min.*, **13**, 306—307).—This mineral was sent by Count N. P. Ignatieff for analysis in the Russian Government Laboratory. It was found in the Bachmut district of the Government of Ekaterinoslav, South Russia, occurring in the form of white, reniform concretions lying in white sand. Analysis gave the following results :—

H_2O.	SiO_2.	Al_2O_3.	SO_3.	P_2O_5.	FeO.	CaO.	MgO.
0·45	3·33	36·39	30·57	3·83	0·32	1·40	0·23

K_2O.	Na_2O.	C.	H_2O.	Total.
6·37	2·89	1·50	12·72	100·00

These results show that the new mineral resembles aluminite or loewigite. The author is of opinion that the mineral may be of practical importance, as, on account of its low percentage of iron, it is adapted, like bauxite, for the preparation of aluminium sulphate. B. H. B.

A Mineral associated with the Columbite of the Val Vigezzo. By A. Piccini (*Zeit. Kryst. Min.*, **13**, 302).—The crystallised substance examined, resembles externally the columbite of the same locality, Craveggia in the Val Vigezzo (Abstr., 1885, 732). The powder is brown with a specific gravity of 5·7. On ignition, it does not change in colour, and loses but little weight. The proportion of

metallic anhydrides is much less in this mineral than in columbite, and consists for the most part of tantalic anhydride, with a considerable quantity of titanic anhydride and a small quantity of niobic anhydride. The bases are principally the cerite and gadolinite earths, a small quantity of ferrous oxide, less manganous oxide, with appreciable quantities of thorium. In columbite, on the other hand, large amounts of ferrous and manganous oxides are found, with traces only of the rare earths. The mineral examined is consequently not columbite, but rather a tantalate of the rare earths, of which the composition would be the same as that of samarskite were the niobic acid not replaced by tantalic acid. B. H. B.

The Peridote of Schaelinger Matten. By A. Knop (*Zeit. Kryst. Min.*, **13**, 236—241).—A yellow mineral occurring in the limestone of Schelinger Matten in the Kaiserstuhl was described by H. Fischer in 1865 as monticellite. The mineral, which may be termed peridote, occurs in association with magnoferrite, koppite, apatite, and barytobiotite. On the crystals, the forms $\infty\bar{P}2$, ∞P, $\bar{P}2$ were observed. An analysis of carefully purified mineral gave the following results (I):—

	SiO_2.	MgO.	FeO.	MnO.	CaO.	Total.
I.	41·88	49·83	4·56	1·73	0·00	98·00
II.	42·41	53·30	2·33	—	—	98·04

In the analysis (I), a small quantity of alumina was found, but not weighed. The results of the analysis and of the crystallographical examination indicate that this variety of peridote is forsterite. An analysis (II) of that mineral from Monte Somma is added for comparison. B. H. B.

Glaucophane. By B. Koto (*Chem. Centr.*, 1887, 391—392).—Lavender-coloured glaucophane occurs in large amount in the Island of Shikotu, together with iron epidote, yellowish-green garnet, and manganese epidote. Analysis gave following numbers:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.
56·71	15·14	7·98	4·31	4·80	4·33	4·83	0·25

Sp. gr. = 2·991. Secondary glaucophane from augite minerals is more frequent. The transformation of pyroxene into blue hornblende and the formation of glaucophane is seen in various stages with formation of more or less glaucophane asbestos. N. H. M.

Altered Cordierite from Rocca Tederighi in Tuscany. By E. Scacchi (*Zeit. Kryst. Min.*, **13**, 297).—This altered product is found in liparite in the form of opaque, greyish-green columns 3 to 5 mm. in length. The axial ratio is $a : b : c = 0{\cdot}58007 : 1 : 0{\cdot}55890$. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
49·62	27·41	8·89	3·95	1·25	8·43	99·55

The specific gravity is 1·616. This product of the alteration of cordierite is evidently pinite. B. H. B.

Composition of Rocks and Minerals from Vulture and Melfi. By L. Ricciardi (*Gazzetta*, **17**, 214—225).—The Vulture is an extinct volcano forming the principal centre of eruptions, probably prehistoric, situated in Apulia; subsidiary craters are Braida and Melfi, the latter of which has been the centre of several disastrous earthquakes. In the paper, a series of analyses are given of the rocks and minerals from the Vulture as also of Melfi. The eruptive material of the former consists principally of cinerea and augite, beside which are found crystals of black mica, leucite, and magnetite, and titaniferous ironstone; on the summit oolite is found. The volcano of Melfi is in all probability a centre of eruption independent of that of the Vulture; the minerals are somewhat similar, although the analyses of the lava and tufa show marked differences. The author agrees with the conclusions of Palmieri and Scacchi, in considering that the three volcanic regions of the Campania, namely, of the Monte di Somna, together with Vesuvius, the region of the Flogrea, and the Roccamontine district, in which the above volcanos are situated, form distinct centres, each with their peculiar characteristics.

V. H. V.

Meteorite from Angra dos Reis. By E. Ludwig and G. Tschermak (*Chem. Centr.*, 1887, 647).—The meteorite which fell at Angra dos Reis, a town on the coast in the province of Rio, Brazil, belongs to a small group of meteorites rich (93·28 per cent.) in augite; small quantities of olivine and of magnetic oxide of iron are also present. The specimen was of sp. gr. 3·43, but not very coherent. The augite had the following composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
42·72	8·84	2·47	6·88	8·95	22·37	0·26	0·19

According to Rose's classification of meteorites, the specimen is akin to howardite and eukrite, differing, however, from both by the chemical and physical properties of the augite, as also from the former by the presence of olivine, and from the latter by the absence of plagioclase. V. H. V.

Flitwick Water. By W. Johnstone (*Analyst*, **12**, 90—92).—This water rises through a bed of ferruginous peat on Flitwick Moor. It appears to result from the percolation of rain-water through the ferruginous sands and peat of the district, until stopped by the Oxford clay forming the floor of the valley. A sample collected in May, 1885, contained in 1000 parts:—

Ammonium oxide	0·1144
Calcium oxide	0·0640
Magnesium oxide	0·0511
Ferric oxide	1·2212
Alumina	0·0044
Cupric oxide	0·0075
Manganous oxide	0·0014
Potassium oxide	0·0024
Sodium oxide	0·0211
Chlorine	0·0340
Sulphuric acid (SO_3)	1·7328
Silica	0·2328
Organic matter	1·2753
	4·7624

Specific gravity at 15·5° = 1·0041.

About two-thirds of the iron is as ferric sulphate; the remainder is in combination with organic acids. The composition is not constant, ferrous as well as ferric salts being sometimes present. When exposed to the air, it deposits a tufaceous bog-iron ore. M. J. S.

Organic Chemistry.

Detection of certain Hydrocarbons in Alcohols. By H. N. Warren (*Chem. News*, **56**, 64).—A sample of wood-naphtha saturated with calcium chloride and fractionated, yielded a fraction boiling at 160—180°, which assumed a fine blood-red colour on the addition of an alkali, baryta with soda being the best for the purpose. This substance was also detected in several samples of light petroleum, methyl amyl and other alcohols, and amongst the products of the action of chlorine on coal-gas. It has not been further examined.

D. A. L.

Ethyl Isobutyl Ether. By A. Meissler (*Chem. Centr.*, 1887, 479).—Ethyl isobutyl ether is contained in that fraction of the product of the action of alcoholic potash on isobutyl bromide which boils at 60—115°. Sodium dissolved in ethyl alcohol also acts on isobutyl chloride, but much more slowly than in the case of the bromide.

N. H. M.

So-called Allyl Trisulphide. By R. Nasini and A. Scala (*Gazzetta*, **17**, 236—240).—In the course of the action of sodium amalgam on a mixture of ethyl iodide and carbon bisulphide, Löwig and Scholz (*J. pr. Chem.*, **79**, 441) obtained a liquid of disagreeable odour, to which they ascribed the formula $C_6H_{10}S_3$, or $(C_3H_5)_2S_3$, regarding it as an allyl-derivative. Their results have not at present been controverted, although several writers of manuals have doubted

the validity of their conclusions. Accordingly, the authors have repeated the experiments, and find that provided all the materials and containing vessels are dry, the only reaction occurring is that between the sodium amalgam and the ethyl iodide; in the presence of moisture, however, a product is obtained similar to that obtained by Löwig and Scholz. Analysis points to a formula, $C_5H_{10}S_3$, or that of diethyl trithiocarbonate, $CS(SEt)_2$; this substance when heated slowly is decomposed into ethyl sulphide and carbon bisulphide; but if heated more rapidly it turns brown at 180°, beginning to distil with decomposition; the greater part, however, distils at 240°, as noted by Schweizer, Debus, and other observers. V. H. V.

Ethereal Oil of Allium Ursinum. By F. W. Semmler (*Annalen*, **241**, 90—150).—The ethereal oil of *Allium ursinum* consists essentially of vinyl sulphide, but it also contains polysulphides of vinyl and minute quantities of a mercaptan and aldehyde. *Vinyl sulphide* is freed from admixture with these substances by the action of metallic potassium. It is a volatile liquid boiling at 101°. Its sp. gr. is 0·9125. Its odour resembles that of allyl sulphide. By the action of dry oxide of silver on the sulphide, *vinyl oxide*, $(C_2H_3)_2O$, is obtained, but it could not be completely separated from unaltered sulphide. The oxide boils at 39°. If moist oxide of silver is substituted, vinyl alcohol, $C_2H_3{\cdot}OH$, is formed, which at once changes into acetaldehyde.

On oxidation with nitric acid, potassium permanganate, or chromic acid, vinyl sulphide splits up, yielding sulphuric and oxalic acids and carbonic anhydride. When a concentrated alcoholic solution of mercuric chloride is cautiously added to an alcoholic solution of vinyl sulphide, crystals are suddenly deposited. If the mercuric chloride is added too rapidly and in excess, the crystals will only separate after diluting the solution with water. If too much water is added, a voluminous, amorphous precipitate will be produced. The crystalline compound is soluble in absolute alcohol. Its formation is represented by the following equation: $2(C_2H_3)_2S + 2HgCl_2 = 2C_2H_3Cl,HgCl_2,(C_2H_3)_2S,HgS$. Allyl sulphide forms an analogous compound with mercuric chloride. If these mercury compounds are heated with potassium thiocyanate, the thiocarbimides of allyl and vinyl respectively are produced.

The precipitate deposited on mixing alcoholic solutions of vinyl sulphide and platinum chloride is analogous in composition to the allyl compound described by Wertheim. Its formation is represented thus: $3(C_2H_3)_2S + 2PtCl_4 = 4C_2H_3Cl,PtCl_4,(C_2H_3)_2S,PtS_2$. With silver nitrate, vinyl sulphide forms a double salt, $(C_2H_3)_2S,2AgNO_3$, analogous to the allyl sulphide compound. It melts about 87°, and turns yellow when treated with water. Vinyl sulphide absorbs bromine, forming the compound $(C_2H_3Br_2)_2SBr_2$, which boils with decomposition at 195°. W. C. W.

Formation and Properties of Inosite and its Occurrence in the Vegetable Kingdom. By R. Fick (*Chem. Centr.*, 1887, 452—453).—Inosite is prepared by treating the fresh plant material with hot alcohol, and keeping the whole in a closed vessel in a warm

place for several days. The alcoholic solution is then separated, distilled, and the small aqueous residue purified by means of lead acetate, precipitated with basic lead acetate, and this precipitate, after being washed, is decomposed with hydrogen sulphide. The filtrate is evaporated down, mixed with alcohol and left to crystallise. The presence of inosite is detected by means of Seidel's reaction (evaporating the solution to dryness with nitric acid, dissolving the residue in water, and adding a few drops of a solution of strontium acetate), a distinct violet coloration with a slight green lustre is obtained, when only 0·3 mgrm. of inosite is present. A large number of plants were found to contain inosite, but only in small amount.

Inosite melts at 225° (corr.), dissolves in 7·5 parts of water at 17—21°; it does not ferment, and cannot be converted into a fermentable sugar by acids. The *acetyl-compound*, $C_6H_7O_6Ac_5$, melts at 215·68° (corr.), distils without change, and is soluble in alcohol, insoluble in water. N. H. M.

Alcoholic Fermentation of Milk-sugar. By P. Vieth (*Analyst*, **12**, 2—6).—The addition of yeast to milk or to a solution of milk-sugar does not set up alcoholic fermentation readily. Under the influence, however, of a special ferment known as kefir grains, milk undergoes a somewhat rapid alcoholic as well as lactic fermentation. These grains contain a bacillus, named *Diospora caucasica* by Kern, and a modified form of *Saccharomyces cerevisiæ* (Abstr., 1883, 226; compare also Struve, Abstr., 1884, 1235). Alcohol is slowly developed when whey or milk is kept in closed vessels, and the marked diminution in the amount of solid residue which occurs when small quantities of milk are exposed to the air for a few days in a warm place, seems also to be due to alcoholic fermentation. M. J. S.

Aldehyde Resin. By E. Puchot (*Ann. Chem. Phys.* [6], **9**, 422—432).—Aldehyde resin washed two or three times with warm water and exposed to air becomes hard and friable. It dissolves in alcohol and is reprecipitated by water. Analysis of two preparations gave the formula $C_{48}H_{64}O_{10} \pm nH_2O$, n being equal to 4, but the amount of water is variable. When exposed to dry air, the resin gives off water, and its weight gradually reaches a minimum at which it remains constant for some time, and then increases. When the weight is at the minimum, the substance has the composition $C_{48}H_{64}O_{10} = 8(C_6H_8O) + O_2$, which varies slightly with the rate of drying. When the increase in weight has become constant, the composition is $C_{48}H_{64}O_{12} = 8C_6H_8O + O_4$. If the resin is exposed to moist air, its weight increases, and becomes constant after some weeks; if it is then exposed to dry air, the weight diminishes until it reaches a new limit. The composition at this last stage is not constant, but approximates to $C_{48}H_{64}O_{12}$. The substance formed in contact with moist air is probably a hydrate, but its composition was not determined.

In some cases, the crude resin was first placed in dry air, then before the loss of weight was complete, in moist air, and finally in dry air again. After this treatment, it had the composition $C_{48}H_{66}O_{13} = C_{48}H_{64}O_{12} + H_2O$, but this result was not constant. In another case,

the composition was $C_{48}H_{64}O_{12}$. The change of weight which the resin undergoes shows that the increase of weight is not due to simple combination with oxygen, but there is simultaneous loss of carbon, increased weight being always less than corresponds with the increased percentage of oxygen. Either of the resins first mentioned increases in weight in moist air, but regains its original weight in dry air, the hydrate formed under the first conditions being decomposed in the dry air. Hydrates are obtained containing 2, 3, 5, or 7 mols. H_2O.

The resin was placed alternately several times in dry air and in air saturated with the vapour from a saturated solution of sodium chloride. The dry substance had the composition $C_{48}H_{68}O_{14}$. In the moist atmosphere, there is an increase in the percentage of oxygen, but a decrease in the percentge of carbon, which may be due either to formation of a hydrate or to oxidation with simultaneous loss of carbon.

From these results, it follows that crude aldehyde resin loses water, and forms the compound $C_{48}H_{64}O_{12}$ or $8(C_6H_8O) + O_2$, which may be regarded as an oxidised polymeride of trialdane. This substance yields more highly oxidised products which may be regarded as hydrated oxides of the same aldane. Members of the latter series absorb water from a moist atmosphere, and form hydrates which decompose in dry air. When aldehyde resin is gradually heated from 120° to the boiling point of sulphur, it undergoes condensation. Water and an oily liquid are given off, and a non-volatile residue containing a high percentage of carbon is left in the retort. C. H. B.

Chloracetones. By C. Cloez (*Ann. Chim. Phys.* [6], **9**, 145—221).—The author has prepared and examined all the chlorine-derivatives of acetone which are theoretically possible if the generally accepted formula is correct. A short history of the derivatives previously known is given, together with full bibliographical references.

The material employed was commercial acetone purified by fractionation and conversion into the hydrogen sodium sulphite compound. The author investigated the action of chlorine: (1) on cold acetone; (2) on acetone which at first was cold but afterwards was heated to 100°; (3) on well-cooled acetone containing iodine; and (4) on boiling acetone containing iodine. No advantage is gained by the presence of iodine, and in fact the iodo-products which are formed in small quantity decompose during distillation and render purification very difficult. The iodine cannot be removed by means of iron or mercury. All fractions boiling above 125—130° should be distilled under reduced pressure. The final product in all four cases is tetrachloracetone.

Monochloracetone is most readily prepared by Barbaglia's method (*Ber.*, **7**, 467) of passing chlorine into well-cooled acetone for several days; a current of water is sufficient for this purpose, a freezing mixture is not necessary. It boils at 117—118°; sp. gr. at 13° = 1·158. It is very slightly soluble in water, but dissolves in all proportions in alcohol, ether, and chloroform. It does not form a crystalline hydrate, and volatilises readily in water-vapour. When freshly prepared, it has no irritating odour, but after exposure to air for some days it gives off

irritating vapours. It can, however, be purified by washing with a very dilute solution of an alkali.

Monochloracetone is readily attacked by chlorine in the cold. Bromine has little effect in the cold, but at 100° energetic reaction takes place with formation of chlorotribromacetone. With potassium, it forms potassium chloride, together with red and brown products which probably contain the acetyl carbinol obtained by Emmerling by the action of potassium or potassium carbonate on bromacetone. Ammonia produces ammonium chloride and the amido-derivative, $COMe{\cdot}CH_2{\cdot}NH_2$, which when distilled with potash yields methylamine. It follows that monochloracetone has the constitution $COMe{\cdot}CH_2Cl$.

The action of a warm concentrated solution of potash on dichlorhydrin yields a liquid closely resembling monochloracetone in its physical properties. It boils at 118—119°; sp. gr. at 11° = 1·194. It combines with hydrochloric and acetic acids, forming derivatives of glycerol, and it also combines with water. With alcoholic ammonia, it yields the badly defined compound hemichlorhydramine, $C_3H_{12}ClNO_2$; this is evidently not an acetone-derivative, and it most probably has the constitution $CH_2Cl{\cdot}CH<\begin{matrix}CH_2\\O\end{matrix}>$.

Dichloracetone is best prepared by the prolonged action of chlorine on well-cooled acetone. It boils at 120°, whilst the monochloro-derivative boils at 117°, but the two compounds may be separated by taking advantage of the fact observed by Mulder and by Barbaglia, that the product obtained under these conditions has the composition of the dichloracetone even in the fraction boiling at 170°. The fraction boiling at 125—170° is collected separately and purified by further fractionation. The pure compound boils at 120°; sp. gr. at 15° = 1·234. It combines readily with sodium hydrogen sulphite, and the compound crystallises with 3 mols. H_2O. Even when carefully purified, the vapour acts energetically on the eyes, &c., but after some time the organs become insensitive to its action. Ammonia acts rapidly on dichloracetone, with formation of ammonium chloride and the base $COMe{\cdot}CHCl{\cdot}NH_2$, which yields methylamine when distilled with potash.

The product of the action of chlorine on cooled acetone has the composition of the dichloro-derivative even in the fraction boiling at 170°, but on redistillation the boiling point is reduced to 120°. Barbaglia obtained a liquid which boiled at 165—170°, and when cooled solidified to a mass of bulky, prismatic crystals melting at 44°. In its physical properties, this product resembles symmetrical dichloracetone, but with bromine it yields a dichlorodibromacetone identical with that obtained from unsymmetrical dichloracetone, and very different from the corresponding compound obtained from the symmetrical derivative. This high boiling fraction may be a polymeride.

Symmetrical dichloracetone is obtained by the action of silver chloride on the symmetrical diiodoacetone prepared by the action of iodine chloride on acetone in presence of water. It has a pungent odour, forms crystals which melt at 44°, and boils at 170° without decomposition.

When dichlorhydrin is oxidised by means of a well-cooled mixture of sulphuric acid and potassium dichromate, in the manner described by Grimaux and Adam, it yields a liquid which has the composition of dichloracetone. When this product is cooled, it crystallises in large needles melting at 43—44°, which change spontaneously, especially in presence of ether, into short prisms with the same melting point. It boils at 170°, has a very pungent odour, and in ethereal or alcoholic solution is a most powerful caustic, producing very severe burns. With ammonia, it forms an unstable compound which crystallises in large plates.

In diffused daylight, chlorine acts somewhat slowly on epichlorhydrin. When the product is distilled and the fraction boiling at 160—180° is purified, it yields a liquid which boils at 170° and has the composition $CHCl_2{\cdot}CH{<}^{CH_2}_{O}{>}$, and is therefore an isomeride of dichloracetone. With ammonia at a low temperature, it yields a white, amorphous, unstable substance, almost insoluble in water, alcohol, and ether; this has the formula $C_6H_4Cl_2NO_2$, but its constitution could not be determined.

The dichloracetone obtained from diiodoacetone is not identical with the so-called symmetrical dichloracetone obtained by the oxidation of dichlorhydrin. The action of bromine, potash, or oxidising agents on dichlorhydrin yields derivatives which closely resemble derivatives of the acetones, but are never identical with them. Potash yields epichlorhydrin, which closely resembles monochloracetone in its physical properties. Bromine yields a derivative to which the constitution $CO(CHClBr)_2$ has been assigned. A compound, $CHCl_2{\cdot}CO{\cdot}CHBr_2$, can also be obtained from acetone. If the two compounds are treated with mercuric chloride the latter yields tetrachloracetone, whilst the former yields a compound containing a lower percentage of chlorine.

If ordinary dichloracetone and the symmetrical dichloracetone from the iodo-derivative are treated with bromine, they both yield dichlorodibromacetones, and when the latter are treated with mercuric chloride the same symmetrical tetrachloracetone is obtained in both cases. When the pseudodichloracetone from dichlorhydrin is treated in the same way, the product is an isomeride of tetrachloracetone, very distinct from either of the compounds $CO(CHCl_2)_2$ and $CCl_3{\cdot}CO{\cdot}CHCl$. Since only two tetrachloracetones can exist, it follows that the derivative from dichlorhydrin is not an acetone-derivative. Again, when dichloracetone and the pseudodichloracetone are subjected to the action of chlorine in sunlight, the products are very different, although both have the composition of pentachloracetone. Only one pentachloracetone is, however, possible. The pseudodichloracetone is a derivative of dichlorhydrin, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$, and has the constitution $CH_2Cl{\cdot}CH{<}^{CHCl}_{O}{>}$, analogous to that of epichlorhydrin. Pseudodichlorhydrin does not combine with acetic acid. It reacts violently with concentrated hydrochloric acid, but when the product is evaporated over sulphuric acid the original compound is obtained.

Trichloracetones.—When a limited quantity of bromine is allowed

to act on dichloracetone, the product $CHCl_2{\cdot}CO{\cdot}CH_2Br$ is obtained, which boils at 111° under a pressure of 25 mm., and when this is heated with mercuric chloride in presence of alcohol, trichloracetone boiling at 172° is obtained. This trichloracetone yields no chloroform with aqueous or alcoholic ammonia, and no phenylcarbylamine with aniline and potash. It therefore does not contain the group CCl_3, and must have the constitution $CHCl_2{\cdot}CO{\cdot}CH_2Cl$. Only a very small quantity was obtained.

Trichloracetone, $CCl_3{\cdot}CO{\cdot}CH_3$, is readily obtained by the action of chlorine on an aqueous solution of sodium citraconate heated at 100° (Gottlieb and Morawsky, *J. pr. Chem.* [2], **12**, 369). With ammonia, it yields chloroform and a small quantity of ammonium chloride, together with a large quantity of acetamide if the liquid has been kept cool and excess of ammonia has been avoided.

The action of chlorine on impure methyl alcohol (Bouis) or on acetone (Bischoff) yields a liquid which has the composition of trichloracetone and boils at 172°; sp. gr. 1·418. It solidifies incompletely in long needles at −14°, the temperature rising suddenly to −5°. The crystals melt between −5° and +2°. It combines with 2 mols. H_2O, forming a hydrate which melts at 43—44°. It also combines with sodium hydrogen sulphite, but the product crystallises with great difficulty. With aniline and potash, it yields phenylcarbylamine; but with ammonia it yields very little if any chloroform or acetamide, ammonium chloride, however, is formed in large quantities, and if the liquid is distilled with potash, it yields dichloromethylamine, which is doubtless derived from the compound $CHCl_2{\cdot}CO{\cdot}CH_2{\cdot}NH_2$. It would follow that the trichloracetone has the constitution $CHCl_2{\cdot}CO{\cdot}CH_2Cl$, but the formation of chloroform and phenylcarbylamine, and the variable boiling and melting points of the compound, show clearly that it is a mixture of a solid trichloro-derivative which melts about −5°, with an isomeride which is liquid even at low temperatures.

Unsymmetrical tetrachloracetone was obtained by Bouis by the action of chlorine on wood-spirit in diffused daylight (*Ann. Chim. Phys.* [3], 21—111), and by Bischoff by the action of chlorine on a mixture of acetone and methyl alcohol (this Journal, 1876, i, 558). It is most readily obtained by passing chlorine into commercial acetone, the temperature being allowed to rise. Tetrachloracetone is a colourless liquid which boils at 180—182°, and becomes brown when exposed to air and light; sp. gr. at 17° = 1·482. When distilled under the ordinary pressure, it undergoes partial decomposition. It is very hygroscopic, and forms a tetrahydrate which melts without decomposition at 30°. With aniline and potash, it yields phenylcarbylamine, and with aqueous ammonia at a low temperature it yields chloroform and monochloracetamide. It therefore has the constitution $CCl_3{\cdot}CO{\cdot}CH_2Cl$.

By the prolonged action of chlorine on pure acetone at first cooled and afterwards heated on a water-bath, Grabowsky (this Journal, 1876, i, 557) has obtained trichloromethyl propyl ketone, boiling at 186°. The author has been unable to obtain this result. Probably the nature of the reaction depends on the purity of the acetone.

Symmetrical tetrachloracetone.—Dichlorodibromacetone prepared by the action of bromine on unsymmetrical dichloracetone is heated

with alcohol and mercuric chloride in sealed tubes at 100°. The product is distilled, and is purified from mercury by conversion into a hydrate which is repeatedly recrystallised, and then decomposed by hydrochloric acid. The product is dried over calcium chloride, and boils at 179—181°; its sp. gr. is the same as that of the preceding compound. With water, it forms a hydrate crystallising in needles which melt at 47—48°. With ammonia or aniline, it yields no distinct result, but neither chloroform nor phenylcarbylamine is formed. The compound therefore does not contain the group CCl_3, and must have the constitution $CHCl_2{\cdot}CO{\cdot}CHCl_2$.

The dichlorodibrom-derivative obtained by the action of bromine on dichlorhydrin yields with mercuric chloride an oily liquid which has no fixed boiling point, and is not attacked by ammonia at the ordinary temperature. It is not a tetrachloracetone.

When the product of the oxidation of dichlorhydrin is treated with bromine, it yields an isomeride of dichlorodibromacetone, which, according to Markownikoff, has the constitution $CHClBr{\cdot}CO{\cdot}CHClBr$. When this compound is treated with mercuric chloride, however, it yields a liquid which fumes in the air, boils at about 180°, has a disagreeable odour, and does not combine with alkaline hydrogen sulphites. With ammonia or aniline, it yields neither chloroform nor phenylcarbylamine, but dichloracetamide and dichloracetanilide respectively. It follows that either there are two isomeric symmetrical tetrachloracetones, or that the product of the oxidation of dichlorhydrin is not an acetone-derivative, as already indicated.

When symmetrical iodacetone is treated with silver chloride, and the product is treated with bromine and afterwards with mercuric chloride, a liquid is obtained which boils at 180°, and is identical with symmetrical tetrachloracetone. The dichloracetone from iodacetone has always been regarded as identical with Markownikoff's products, but these results show that they are very different, and the latter is most probably a derivative of epichlorhydrin—

$$CH_2Cl{\cdot}CH{<}\begin{matrix}-O-\\ CHCl\end{matrix}{>}.$$

Pentachloracetone was obtained by Staedeler by adding hydrochloric acid to a boiling solution of quinic acid and potassium chlorate. The yield is very small, and great care is required to avoid explosions. Much better results are obtained by the following method. A solution of citric acid in 1·5 parts of water is allowed to fall drop by drop down a tube packed with pumice, up which passes a current of dry chlorine, the tube being heated at 100° by means of a water-jacket. The product is purified by washing and redistillation. If the water used for washing is evaporated at a low temperature, it deposits crystals of citric acid which contain 2 mols. H_2O, and are quite different in appearance from the ordinary crystals. They form flattened prisms with four of the faces abnormally developed. The cleavage planes and the angles at the edges are, however, identical with those of the ordinary crystals.

The pentachloracetone obtained is identical with that prepared by Staedeler and by Cloez, sen., by the action of chlorine on alkaline

citrates. With ammonia, it yields chloroform and dichloracetamide, and with aniline it yields phenylcarbylamine and dichloracetanilide. It may also be prepared in large quantity by the action of dry chlorine on dry commercial acetone in direct sunlight. Pure acetone seems to give a different result, since Fittig, and Dumas and Kane, obtained no derivative higher than the dichloracetone by the action of chlorine on acetone at 100° or in sunlight. Under the conditions given, however, the acetone is converted into a mixture of pentachloracetone and hexachloracetone which are separated by fractionation.

Pentachloracetone is a colourless liquid with an odour resembling that of chloral, which, however, is only observed after the liquid has been exposed to air. It boils at 192°, and is readily volatile in water vapour; sp. gr. at 14° = 1·576. It dissolves in 10 parts of water, from which it separates completely at 50—60°. At low temperatures, the solution deposits a tetrahydrate in small, rhomboidal plates melting at 15° with decomposition. With ammonia, it yields chloroform and dichloracetamide.

The action of chlorine in sunlight on the pseudodichloracetone from dichlorhydrin yields a liquid which has a pungent smell, and boils at 185°; sp. gr. at 8° = 1·617. With ammonia, it yields trichloracetamide but no chloroform, and hence it is not a derivative of acetone. The action of chlorine on dichloropropylene oxide yields a strongly fuming liquid which boils at about 178°. Its composition does not agree very well with that of pentachloropropylene oxide, and when treated with ammonia, it yields trichloracetamide but no chloroform. It therefore has the constitution $CHCl_2 \cdot CCl<^{CCl_2}_{-O-}>$. From these results, it is evident that there are three isomeric compounds having the composition of pentachloracetone, but only one of these is really a derivative of acetone.

Hexachloracetone was obtained by Plantamour by the action of chlorine on a solution of citric acid in sunlight, and has been described under different names by Laurent, Staedeler, and Cloez, sen. A solution of citric acid is treated with chlorine in sunlight until the gas is no longer absorbed. Carbon dioxide is given off, especially in the later stages of the reaction. The yield is about one-fourth of the weight of the citric acid taken. Hexachloracetone can readily be obtained by the action of chlorine on acetone in sunlight. The fraction of the product which boils at 185—220° is collected and purified. The fraction boiling at 290° contains a considerable quantity of hexachlorobenzene, which is probably formed by pyrogenic decomposition, and does not exist in the product before distillation. It is not always formed.

Hexachloracetone is a very limpid liquid with an odour which is feeble at a low temperature, but becomes very pungent and irritating when the liquid is warmed. It boils without decomposition at 202—204°, and when cooled solidifies in large, white plates melting at −2°; sp. gr. at 12° = 1·744; vapour-density 9·615. It is slightly soluble in water, and forms a crystalline monohydrate which is almost insoluble in water. With aqueous ammonia it yields chloroform and trichlor-

acetamide, and with aniline it yields chloroform and trichloracetanilide. When heated with water in sealed tubes at 120°, it splits up into chloroform and trichloracetic acid. The action of chlorine on epichlorhydrin in sunlight yields crystals which seem to be hexachlorobenzene, and a small quantity of a liquid which boils at 200—210° and yields chloroform and trichloracetamide with ammonia. Most probably the product has the constitution $CCl_3 \cdot CCl<^{CCl_2}_{-O-}>$.

Chlorobromacetones.—Theegarten (this Journal, 1874, 242) treated epichlorhydrin with bromine, and oxidised the product. In this way, he obtained crystals which have an irritating odour, melt at 34—35°, and boil at 177—180°. This compound is only slightly soluble in water, but dissolves readily in alcohol and ether. It does not combine with bisulphites, and doubtless has the constitution

$$CH_2Cl \cdot CH<^{CHBr}_{-O-}>.$$

A compound with the composition of monochlorotribromacetone was obtained by Claus and Lindhorst (Abstr., 1880, 862) by the action of bromine and water on dichlorhydrin, and by Grimaux and Adam (*ibid.*, 457) by the action of bromine on epichlorhydrin at 100°. With equal molecular proportions of bromine and epichlorhydrin, the reaction is complete in a few hours. The product is a colourless, pungent liquid, heavier than water, with which it forms a hydrate melting at 55°, soluble in alcohol, and stable when exposed to air. The compound itself decomposes when boiled even under reduced pressure. It is not a true derivative of acetone, but is derived from epichlorhydrin.

When monochloracetone is heated with bromine at 100° and the product dissolved in water, a tetrahydrate is formed which can be recrystallised. It is decomposed by hydrochloric acid, and when the liquid thus obtained is dried, it boils at 130° under a pressure of 25 mm., and at 215° under normal pressure; sp. gr. = 2·270. It has a pungent, irritating odour. The hydrate is only slightly soluble in water, but dissolves more readily in alcohol of 80°, from which it crystallises in large, hexagonal tables containing 1 mol. H_2O; this is readily given off even on exposure to the air. With aqueous ammonia at a low temperature, chlorotribromacetone yields bromoform and chloracetamide, and therefore has the constitution $CBr_3 \cdot CO \cdot CH_2Cl$. So-called dichlorodibromacetone, obtained by the action of bromine on pseudodichloracetone, is a liquid which solidifies at −14°, melts at −8°, and boils at 135° under a pressure of 40 mm. It does not combine with alkaline hydrogen sulphites. It forms a tetrahydrate, which crystallises in long prisms melting at 53—54° with partial decomposition. The action of ammonia shows that this compound contains neither CCl_2Br nor CBr_2Cl, and hence its constitution must be $CHBrCl \cdot CH<^{CBrCl}_{-O-}>$.

The action of bromine on dichlorhydrin yields a compound which boils at 140—141° under a pressure of 20 mm. It forms a crystalline tetrahydrate which melts at 55—56°, and boils with partial decompo-

sition at 140—150° under a pressure of 20 mm. It is not identical with the preceding compound, and may have the constitution

$$CBr_2Cl\cdot CH<\begin{matrix}CHCl\\ O\end{matrix}>.$$

The action of bromine on ordinary dichloracetone yields a liquid which boils at 120° under a pressure of 25 mm., and does not solidify at a low temperature. It forms a tetrahydrate which crystallises in hexagonal tables with a very disagreeable odour; these readily lose their water. Barbaglia's dichloracetone boiling at 170° yields the same derivative with bromine, and is therefore a polymeride of ordinary dichloracetone. Dibromodichloracetone reacts energetically with ammonia, but no chlorobromoform is produced, and hence the compound must have the constitution $CHCl_2\cdot CO\cdot CHBr_2$. With mercuric chloride, it yields a tetrachloracetone which does not contain the group CCl_3.

When trichloracetone is treated with bromine at 100°, it yields a trichlorobromacetone, which boils at 107° under a pressure of 25 mm., and at 190° under the ordinary pressure. It is very hygroscopic, and forms a tetrahydrate which crystallises in hexagonal tables melting at 48°. With ammonia, it yields chloroform and bromacetamide, and therefore must have the constitution $CCl_3\cdot CO\cdot CH_2Br$.

Tetrabromacetone forms a tetrahydrate, which, although unstable, crystallises readily. With ammonia, it yields bromoform and bromacetamide.

All the chlorobromacetones described are tetra-substitution-derivatives. Starting from tetrachloracetone, each substitution of bromine for chlorine produces a rise of about 10° in the boiling point. There is also a gradual increase in the specific gravity.

Action of Ammonia and Amines on Chloracetones.—The action of orthotoluidine on hexachloracetone yields orthocresyltrichloracetamide, $C_6H_4Me\cdot NH\cdot C_2Cl_3O$, which crystallises in large needles only slightly soluble in cold alcohol. It melts at 66—67°, readily remains in superfusion, and volatilises at 215°. Paratoluidine yields the corresponding para-derivative, which crystallises in very short rectangular prisms, melting at 79—80°, and volatilising with partial decomposition at 185°. It is only slightly soluble in cold alcohol.

With diethylamine, hexachloracetone yields diethyltrichloracetamide, which is very soluble in alcohol, and crystallises in prisms which melt at 90° and volatilise almost immediately with partial decomposition. With trimethylamine, dimethyltrichloracetamide is formed; this is very soluble in boiling alcohol, and crystallises in radiating needles which melt at 104°, and sublime at 195°. With dimethylaniline, the reaction takes place only on warming, and the product is a mixture of a violet colouring matter, soluble in boiling water but almost insoluble in ether, and very soluble in chloroform, with another badly defined colouring matter. Allylamine yields allyltrichloracetamide, soluble in alcohol and in chloroform, and crystallising in large tables which melt at 45° and volatilise without decomposition at 190°. With hexachloracetone and pentachloracetone respectively, ethylenediamine yields the two derivatives, $C_2H_4 : N_2H_3\cdot C_2Cl_3O$

and $C_2H_4 : N_2H_3{\cdot}C_2HCl_2O$. The first is soluble in alcohol, and crystallises in elongated rhomboidal plates which melt at 200° and sublime at the same temperature. The second is soluble in warm alcohol, and very soluble in ether. It crystallises from alcohol in elongated parallelograms, and from ether in fan-shaped plates.

When one molecular proportion of urea is heated at 150° with two molecular proportions of hexachloracetone, the amide—

$$CO : N_2H_2(C_2Cl_3O)_2,$$

is readily obtained. It crystallises from its alcoholic solution in yellowish, hexagonal plates. C. H. B.

Chlorinated Methyl Formates. By W. Hentschel (*J. pr. Chem.* [2], **36**, 209—215).—Continuing his previous work (this vol., p. 1027) the author has repeated Cahours' investigation (*Ann. Chim. Phys.* [3], **19**, 342) on the chlorination of methyl formate, but with totally different results.

The chlorination takes place very slowly in the dark, very rapidly in bright daylight, and care must be taken to prevent an accumulation of the two reacting substances, or violent explosions occur. The author obtained the trichloromethyl chloroformate, $C_2Cl_4O_2$, previously described by him (*loc. cit.*), but could obtain no such stable compound, $C_2Cl_4O_2$, boiling at 180—185°, as is described by Cahours, and usually given in text-books. He believes that such a compound does not exist, and that Cahours must have been mistaken in his results.

L. T. T.

Action of Sodium on Ethyl Salts of the Higher Fatty Acids. By O. Wohlbrück (*Ber.*, **20**, 2332—2340; comp. this vol., p. 717).—*Ethyl dimethylisobutyrylacetate*, $CHMe_2{\cdot}CH{\cdot}CO{\cdot}CMe_2{\cdot}COOEt$, is obtained by adding 30 grams of sodium to 100 grams of ethyl isobutyrate diluted with an equal weight of absolute ether, the whole being kept cool. Afterwards it is heated in a water-bath for some hours. The product is poured into water, and the oil so obtained is treated with dilute aqueous soda, dried and distilled. It is a lemon-yellow liquid of a strong aromatic odour, boiling at 186—189° under 716 mm. pressure.

α-Dimethyl-β-hydroxyisocaproic acid,

$$CHMe_2{\cdot}CH{\cdot}CH(OH){\cdot}CMe_2{\cdot}COOH,$$

is contained as sodium salt in the soda used in purifying the above ethyl salt, and crystallises in prisms melting at 108°. It is soluble in water, readily in ether. The *barium salt* with 3 mols. H_2O forms readily soluble, microscopic plates; the *silver salt* blackens when exposed to light, and gives a mirror when heated in water. The acid is also formed by the reduction with sodium of ethyl dimethylisobutyrylacetate diluted with alcohol.

Ethyl isopropylisovalerylacetate,

$$CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH(CHMe_2){\cdot}COOEt,$$

is prepared by the action of sodium (38 grams) on ethyl isovalerate (100 grams) diluted with dry ether. The product is purified in a manner similar to ethyl dimethylisobutyrylacetate. It is a bright

yellow oil boiling at 204—207 under 722° mm. pressure. When treated with bromine, and the product decomposed by an alkali, an acid melting at 185—187° (probably $C_{10}H_{16}O_3$) is obtained.

α-Isopropyl-β-isobutylhydracrylic acid,

$$CHMe\cdot CH_2\cdot CH(OH)\cdot CH(CHMe_2)\cdot COOH,$$

is contained in the aqueous alkaline extract from ethyl isopropylisovalerylacetate. It is an oil which solidifies after some days to long, slender needles of a silky lustre. It melts at 120°, and dissolves readily in alcohol, ether, and hot water. When heated above its melting point, it sublimes in lustrous needles. The *barium salt* crystallises in hard, colourless prisms. The acid can also be obtained by reducing ethyl isopropylisovalerylacetate with sodium.

N. H. M.

Transformation of Fumaric and Maleïc Acids into Aspartic Acid and Asparagine. By G. Koerner and A. Menozzi (*Gazzetta*, **17**, 226—231).—The authors have shown that paraffinoïd amido-acids can be converted into olefinoïd acids by the introduction of the methyl-group into the amido-residue, and subsequent removal of the elements of the amine. A case of the converse change is here investigated, in that it is shown that ethyl fumarate, when heated with alcoholic ammonia in sealed tubes, yields an oil, ethyl aspartate, and a substance of the composition $C_4H_6N_2O_2$. The ethyl aspartate is a colourless oil, which boils at 150—154° under a pressure of 25 mm., but is decomposed when distilled at the ordinary pressure. The compound $C_4H_6N_2O_2$ crystallises in glistening leaflets melting at about 250° with decomposition; it may be regarded probably as the imide of aspartic acid; on protracted heating with alcoholic ammonia, it is converted into asparagine. The above-mentioned oil when treated with aqueous ammonia yields asparagine in abundance, the crystals formed showing hemihedric modifications.

In like manner, ethyl maleate yields identical products, and practically in the same proportion.

V. H. V.

Oxidising Action of Alloxan. By G. Pellizzari (*Gazzetta*, **17**, 254—259).—When a concentrated aqueous solution of alloxan is added to phenylhydrazine hydrochloride in presence of sodium acetate, nitrogen and benzene vapour are evolved, and alloxantin is formed thus: $2C_4H_2N_2O_4 + NHPh\cdot NH_2 = C_8H_4N_4O_7 + C_6H_6 + N_2 + H_2O$. It is supposed that in the first phase of the reaction two atoms of hydrogen are eliminated in the form of water, with formation of a hypothetical diazobenzene, which decomposes into benzene and nitrogen. If this view were correct, then hydrazobenzene under similar conditions should yield azobenzene, a result confirmed by experiment.

An analogous result was obtained with indigo-white, the alloxan being reduced to alloxantin, whilst simultaneously the white is oxidised to indigo-blue, thus: $2C_4H_2N_2O_4 + C_{16}H_{12}N_2O_2 = C_8H_4N_4O_7 + C_{16}H_{10}N_2O_2 + H_2O$.

Ceresole (Abstr., 1883, 913) has shown that hydroxylamine hydrochloride acts on alloxan in a manner similar to the usual reaction with ketones, leading to the formation of violuric acid. In the paper,

this result is confirmed, and the identity of the product formed with violuric acid is established by crystallographic measurements.

V. H. V.

1 : 3 Methylphenylthiophen and 1 : 2 Thioxen. By C. Paal and A. Püschel (*Ber.*, **20**, 2557—2560).—1 : 3 *Methylphenylthiophen*, C_4SH_2MePh, is obtained when phenyllevulinic acid, or preferably its sodium salt, is heated with phosphorus trisulphide or pentasulphide; the sodium salt must contain water, otherwise carbonisation is the sole result. It crystallises in large, nacreous laminæ, melts at 72—73°, distils without decomposition, and is readily soluble in alcohol, benzene, &c. It is less volatile with steam than its isomerides, has an odour resembling that of diphenyl, and gives the indophenine reaction, but does not show Laubenheimer's reaction distinctly. The *tetrabromo*-derivative, $C_{11}SH_6Br_4$, formed by the action of methylphenylthiophen on an excess of bromine in the cold, crystallises in slender needles or scales, melts at 136—137°, and is readily soluble in ether, benzene, and light petroleum, less so in alcohol and acetic acid.

1 : 2 *Thioxen*, $C_4SH_2Me_2$, is prepared by distilling β-methyllevulinic acid with phosphorus trisulphide, and washing the distillate with ice-cold, dilute, aqueous soda. It is a colourless liquid, which boils at 134—138°, and shows the indophenine and Laubenheimer reactions. The alkaline solution employed for washing the distillate contains 1 : 2 : 4 thioxenol.

W. P. W.

Action of Methyl Chloride on Orthodichlorobenzene in Presence of Aluminium Chloride. By C. Friedel and J. M. Crafts (*Ann. Chim. Phys.* [6], **10**, 411—424).—The action of methyl chloride on dibromortho-xylene in presence of aluminium chloride is very complicated, and no definite products were obtained.

Orthodichlorobenzene, prepared by Istrati, was purified by crystallising out the less fusible para-derivative, and dissolving the orthodichlorobenzene in a mixture of equal vols. of ordinary sulphuric acid and the fuming acid, which leaves the greater part of the still admixed para-derivative undissolved. The sulphonic acid thus obtained was recrystallised and decomposed by heating in a retort into which a current of steam was passed. Some paradichlorobenzene distils over at 100°, and the ortho-derivative passes over in an almost pure condition at about 200°. It boils at 178°; sp. gr. at 0° = 1·3254. During distillation, crystals of the sulphone $(C_6H_3Cl_2)_2SO_2$ condense in the upper part of the condenser; they melt at 173°, and boil at 360° with partial decomposition.

The orthodichlorbenzene was mixed with 20 per cent. of aluminium chloride, heated on a water-bath, and treated with a current of dry methyl chloride for about 10 hours. The chief products are hexamethylbenzene and trichloromesitylene.

Hexamethylbenzene thus obtained crystallises in long needles which melt at 164° and boil at 264°. With an excess of picric acid, it forms a compound containing the two substances in equal molecular proportions, and which crystallises in golden-yellow lamellæ melting at 168—169°.

Trichloromesitylene contains more chlorine than the original com-

pound, although some of the latter always remains unaltered. Its formation is not due to the presence of any trichlorobenzene. It crystallises from alcohol in slender needles, which melt at 205° and boil at 280° without decomposition. When heated in sealed tubes with 16 times its weight of hydriodic acid of sp. gr. 1·9, in the vapour of diphenylmethane, it yields mesitylene. Under the same conditions, hexamethylbenzene yields mesitylene and methane.

The formation of hexamethylbenzene is doubtless due to the reducing action which has been observed in similar reactions. Probably the organo-metallic compound is produced from the dichlorobenzene, with displacement of chlorine and not of hydrogen, and this chlorine produces the trichloromesitylene. Analogous phenomena have been observed by L. Roux in the action of aluminium chloride on the haloïd derivatives of naphthalene.

In addition to hexamethylbenzene, a small quantity of a compound which seems to be a chloromethyl-derivative of diphenyl, is formed.

Aluminium chloride alone has no action on orthodichlorobenzene at 160°. C. H. B.

Action of Methylene Chloride on Methylbenzenes in Presence of Aluminium Chloride. By C. Friedel and J. M. Crafts (*Ann. Chim. Phys.* [6], **11**, 263—277).—Benzene yields toluene, diphenylmethane melting at 25° and boiling at 260—265°, and anthracene. The absence of hydranthracene is due to its reduction to anthracene and methyl chloride by the action of the methylene chloride, the methyl chloride then producing the toluene. The relative quantities of diphenylmethane and anthracene obtained depend on the proportions of methylene chloride and benzene.

Toluene yields a mixture of meta- and para-xylene boiling at 130—150°, ditolylmethane boiling at 280—290°, and dimethylanthracene melting at 231—232°.

Metaxylene, in addition to liquid products, yields tetramethylanthracene melting at 162—163°; this unites with picric acid in equal molecular proportions to form a deep red compound crystallising in stellate groups. Oxidised with chromic acid in presence of acetic acid, it yields yellowish-white prisms which melt at 206°, and have the composition $C_{18}H_{16}O_2$. From its mode of formation this tetramethylanthracene must have the constitution 1′ : 3′ : 1 : 3 or 1′ : 3′ : 2 : 4.

Pseudocumene yields durene and solid products, which melt respectively at about 165°, 220°, and 290°. The first is a small quantity of tetramethylanthracene identical with that obtained from metaxylene. The second consists of hexamethylanthracene, which from its mode of formation must have the constitution 1′ : 2′ : 4′ : 1 : 2 : 4 or 1′ : 3′ : 4′ : 1 : 2 : 4. If it is mixed in alcoholic solution with picric acid, the two substances unite in equal molecular proportions, and the compound separates in small, golden-brown needles which melt at about 203°. The hydrocarbon dissolves in sulphuric acid, forming a red solution, which becomes colourless as the acid absorbs moisture from the air. The third product might be expected to be a hepta- or octamethylanthracene. It has the composition $C_{18}H_{18}$, forms no compound

with picric acid, and yields a dibromo-derivative which has the composition $C_{18}H_{16}Br_2$ or $C_{18}H_{14}Br_2$. When oxidised with chromic acid and acetic acid, it yields yellowish or white needles, which melt at 325° and sublime completely without decomposition at a higher temperature. The composition of this product agrees more nearly with the formula $C_{18}H_{16}O_2$ than $C_{18}H_{14}O_2$. With bromine, a mixture of a mono- and dibromo-derivative is obtained. Most probably the hydrocarbon is an isomeride of tetramethylanthracene, although it differs markedly from it and the other methylanthracenes. C. H. B.

Decomposition of Mixed Ethers by Heat and Nitric Acid. By G. Errera (*Gazzetta*, **17**, 193—209).—In former investigations it has been shown that when the mixed ethers containing a paraffinoïd and aromatic grouping are heated with nitric acid, they yield the corresponding aromatic aldehyde or its nitro-derivative, and the nitrate of the paraffin. Also Liebig, Cannizzaro, and others have shown that when heated, the ethers decompose into an aldehyde and hydrocarbon.

In this paper, the reactions are studied in the case of benzyl isobutyl ether and benzyl isoamyl ether, and halogen-derivatives of benzyl ethyl ether. When benzyl isobutyl ether is heated with concentrated nitric acid, it forms benzaldehyde and isobutyl nitrate, whilst benzyl isoamyl ether yields the same aldehyde and isoamyl nitrate.

Considerable difficulty was experienced in the preparation of parabromobenzyl chloride, whether by the bromination of benzylic chloride or the chlorination of benzylic bromide; the product was invariably a mixture nearly in molecular proportion of parabromobenzylic chloride and bromide. This mixture, however, serves for the preparation of *parabromobenzyl ethyl ether*, $C_6H_4Br\cdot CH_2\cdot OEt$, which is a colourless liquid of fruity odour boiling at 243°, but with appreciable decomposition into parabromobenzaldehyde and ethane; this change is instantaneous at the temperature of boiling sulphur. The bromobenzyl ethyl ether is converted into parabromobenzaldehyde by the action of nitric acid.

Parachlorobenzyl ethyl ether, $C_6H_4Cl\cdot CH_2\cdot OEt$, from parachlorobenzylic bromide, is a liquid of properties similar to those of the bromo-compounds; it boils at 225—227°, and is decomposed at a higher temperature into the corresponding aldehyde and ethane; it also yields the same aldehyde when treated with nitric acid.

V. H. V.

Isonitroso-derivatives. By H. v. Pechmann (*Ber.*, **20**, 2539—2544).—When pure benzaldoxime is shaken with 10 times its volume of a 30 per cent. solution of sodium hydrogen sulphite, a crystalline compound is obtained, which after removal of the mother-liquor and washing with alcohol and ether, crystallises from water in small, white needles of the composition $SO_3Na\cdot CHPh\cdot NH\cdot SO_3Na + 3H_2O$ This compound is insoluble in alcohol but very soluble in water; its aqueous solution is decomposed on boiling. When heated with dilute acids or alkaline carbonates, or when treated with alkalis in the cold, it decomposes quantitatively into benzaldehyde, sodium sulphate, and ammonium hydrogen sulphite.

Acetoxime dissolves in a solution of sodium hydrogen sulphite with

development of heat, and yields a clear liquid from which, on addition of alcohol and some acetic acid, a crystalline compound slowly separates. Dilute acids decompose this compound into acetone, sodium sulphate, and ammonium hydrogen sulphite.

With sodium hydrogen sulphite, under similar conditions, nitrosoacetone forms a compound which most probably has the composition $SO_3Na{\cdot}CMe(OH){\cdot}CH(SO_3Na){\cdot}NH{\cdot}SO_3Na + 3H_2O$. This separates from dilute alcohol as a powder consisting of colourless needles, and is extremely soluble in water but insoluble in alcohol. When heated with dilute acids, it is decomposed into methylglyoxal, sodium sulphate, sodium hydrogen sulphite, and ammonium hydrogen sulphite. The methylglyoxal was recognised by subjecting the product to steam distillation and treating the distillate firstly with phenylhydrazine acetate, when the *phenylhydrazide*, $N_2HPh : CH{\cdot}CMe : N_2HPh$, which crystallises in slender, yellow needles melting at 145°, was obtained; and secondly with toluylénediamine, when methyltoluquinoxaline, identical with that described by Hinsberg (Abstr., 1886, 561), was formed. These derivatives are also formed by the action of these reagents on nitrosoacetone, but their formation in the absence of this compound may be regarded as affording evidence of the presence of methylglyoxal. W. P. W.

Unsymmetrical Secondary Hydrazines. By B. Philips (*Ber.*, **20**, 2485—2488).—Sodium phenylhydrazine suspended in benzene is treated with an alkyl bromide, and the mixture after the lapse of some hours is heated on a water-bath to complete the reaction. The product, after filtration from the sodium bromide, is purified by saturating the benzene solution with hydrogen chloride and filtering from the insoluble hydrochlorides; the benzene is then removed by distillation, the residue dissolved in ether, the solution again distilled, and the base obtained by precipitating the aqueous solution of the hydrochloride with an alkali. The secondary hydrazines when freshly distilled are colourless liquids which become brown in the air, dissolve to clear solutions in concentrated hydrochloric acid, and show all the characteristic properties of Fischer's methyl- and ethyl-phenylhydrazine.

α-Isopropylphenylhydrazine, $NPrPh{\cdot}NH_2$, boils at 185° under 172 mm. and at 233° under the ordinary pressure; the *hydrochloride* crystallises well from benzene and melts at 135°. The *tetrazone* forms colourless crystals and melts at 85°, the *thiosemicarbazide*, $NPrPh{\cdot}NH{\cdot}CS{\cdot}NHPh$, crystallises from alcohol in large, well formed crystals and melts at 116°, and the *acetyl*-derivative, $NPrPh{\cdot}NHAc$, melts at 97°.

α-Isobutylphenylhydrazine, $C_4H_9{\cdot}NPh{\cdot}NH_2$, boils at 193—195° under 179 mm., and at 240—245° under the ordinary pressure, in the latter case with partial decomposition and formation of small quantities of ammonia. The hydrogen sulphate forms nacreous scales.

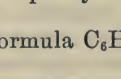
α-Isoamylphenylhydrazine, $C_5H_{11}{\cdot}NPh{\cdot}NH_2$, boils at 210° under 57 mm., and at 260° under the ordinary pressure.

α-Benzylphenylhydrazine (Abstr., 1886, 1025) is a thick, colourless liquid which cannot be distilled without decomposition in a partial vacuum, and when cooled in open vessels gradually solidifies to a

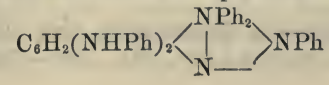
crystalline mass; this melts at 21° and seems to contain 1 mol. H_2O. The anhydrous base does not solidify in dry air. The *acetyl*-derivative melts at 121°, and the *tetrazone* at 109°. When treated with benzaldehyde, *benzylidenebenzylphenylhydrazine*, $C_7H_7{\cdot}NPh{\cdot}N : CHPh$, is obtained; this crystallises in needles, melts at 109°, and is readily soluble in alcohol, ether, and benzene. This base could not be prepared by the direct action of benzyl chloride on benzylidenephenylhydrazine; if, however, the sodium compound of the base, obtained by the addition of finely divided sodium to benzylidenephenylhydrazine in benzene solution, is treated with benzyl chloride, a compound is obtained which shows all the properties of benzylidenebenzylphenylhydrazine. The author regards this result as affording experimental evidence in favour of the formula $NHPh{\cdot}N : CHPh$ for benzylidenephenylhydrazine. W. P. W.

Azophenines and Indulines. By O. Fischer and E. Hepp (*Ber.*, **20**, 2479—2484).—Azophenine can be obtained by heating nitrosomethylaniline and nitrosoethylaniline with aniline hydrochloride (1 part) and aniline (4 to 5 parts) at 80°. The best method of preparation, however, consists in digesting paranitrosodiphenylamine (1 part) with aniline hydrochloride (1 part) and aniline (5 parts) at 100° for 8 to 10 hours; the product, which contains induline and paramidodiphenylamine (m. p. = 66—67°), is washed with water and alcohol, and crystallised from toluene: the yield amounts to 1·5 part of pure azophenine. The azophenine of paratoluidine can also be prepared from nitrosodiphenylamine and paratoluidine, and is identical with Kimich's compound (this Journal, 1876, i, 268).

Chlorazophenine, $C_{36}H_{28}ClN_5$, is obtained from parachloronitrosodiphenylamine by a similar method; it melts at 230°, and closely resembles azophenine in its properties, but is somewhat more soluble in benzene and toluene. *Tetrabromazophenine*, $C_{36}H_{25}Br_4N_5$, results from the action of nitrosodiphenylamine (1 part) on parabromaniline (4 parts) and parabromaniline hydrochloride (1 part) at 100°; it melts at 243°. If metahydroxynitrosodiphenylamine is substituted for nitrosodiphenylamine in the preparation of azophenine, *hydroxyazophenine* is obtained. Dibromonitrosophenol also yields a brominated azophenine when heated at 90° with aniline and aniline hydrochloride. From these results, it is evident that nitrosodiphenylamine enters in some way into the molecule of azophenine, and that the views advanced by Witt with regard to the constitution of this compound (this vol., p. 821) must be abandoned in favour of those originally put forward by Kimich. If paranitrosodiphenylamine be represented as a quinoneoxime-derivative of the formula $C_6H_4<\begin{matrix}NHPh\\|\\N\end{matrix}>O$,



the authors regard the formation of azophenine as analogous to that of quinone-anilide, and attribute to azophenine the formula



[N : NHPh : N : NHPh = 1 : 2 : 4 : 6]. This view may be considered as being confirmed in the following way:—Azophenine when heated with alcoholic ammonium sulphide and toluene at 130—140° for some hours is converted into *dihydrazophenine*, $C_{36}H_{31}N_5$; this crystallises in white needles, melts at 173—174°, and is soluble in alcohol, readily soluble in chloroform and toluene, and insoluble in hydrochloric acid. Moreover, if azophenine is digested with alcohol and concentrated sulphuric acid at 100° in a reflux apparatus, it is converted into a compound, $C_{24}H_{19}N_3O_2$, which crystallises from aniline in silver-grey scales, red by reflected light, dissolves in concentrated sulphuric acid with a magenta colour, and yields with tin and hydrochloric acid, a colourless crystalline reduction compound; aniline and a blue dye are also produced in this reaction.

When nitrosodiphenylamine, aniline, and aniline hydrochloride in alcoholic solution are heated at 120°, two indulines are formed, one of which yields a hydrochloride readily soluble, and the second a hydrochloride sparingly soluble in hot alcohol. The latter is identical with the blue-shade induline obtained from azobenzene and aniline hydrochloride, and is formed in larger proportion by heating at 135—140°, whilst pure azophenine heated with aniline and aniline hydrochloride at 140° is almost wholly converted into it. W. P. W.

Action of Heat on Triethylbenzylphosphonium Salts. By N. Collie (*Phil. Mag.*, **24**, 27—37).—A continuation of the author's researches on the decomposition of phosphonium salts by heat (Proc., 1886, 164). Triethylbenzylphosphonium chloride, prepared by treating triethylphosphine with excess of benzyl chloride, first fuses when heated, and eventually decomposes without charring into ethylene and diethylbenzylphosphine. Triethylbenzylphosphonium bromide decomposes with charring into hydrogen bromide, triethylphosphonium and diethylbenzylphosphonium bromides, acetylene, and other hydrocarbons. Triethylbenzylphosphonium hydroxide gives triethylphosphine oxide and toluene. The hydrogen carbonate when heated decomposes into toluene, carbonic anhydride, and triethylphosphine oxide. The normal carbonate could not be obtained, thus showing the decrease in alkalinity produced by introducing the benzyl-group, the tetrethyl compound forming a normal compound, whilst the tetrabenzyl compound will not fix carbonic anhydride at all. Triethylbenzylphosphonium sulphate decomposes into triethylphosphine oxide, dibenzyl, and sulphurous anhydride, whilst the acetate decomposes partly into triethylphosphonium oxide and methyl benzyl ketone, partly into triethylphosphine and benzyl acetate. The oxalate gave triethylphosphonium oxide, toluene, carbonic anhydride, and carbonic oxide. It is supposed that water took part in this reaction, as no triethylphosphine was produced. These experiments show that when triethylbenzylphosphonium oxy-salts are heated, the benzyl-group is invariably separated from the phosphorus. In the cases of the chloride and bromide, the ethyl-group separates as ethylene. H. K. T.

Action of Bromine on Bromanilic and Chloranilic Acids. By S. Levy and K. Jedlička (*Ber.*, **20**, 2318—2321).—Experiments

made by the authors confirm the result obtained by Hantzsch and Schniter (this vol., p. 925), showing that the product of the reaction between bromine and bromanilic acid is perbromacetone (Stenhouse, *Annalen*, Suppl. **8**, 17). Phenylhydrazine acts on perbromacetone so vigorously that ether has to be used as a diluent; the products of the reaction are phenylhydrazine hydrobromide and bromobenzene. Bromine acts on chloranilic acid with formation of the compound $C_6Br_8Cl_3{\cdot}OH$ (Stenhouse, *loc. cit.*). When 10 grams of the latter is treated with 8 grams of barium hydroxide and 500 c.c. of water and heated to boiling, chlorodibromomethane (6 grams) and barium carbonate, bromide, and chloride are formed. When dry ammonia is passed through a solution of the compound $C_6Br_8Cl_3{\cdot}OH$ in anhydrous ether, chlorodibromomethane and dibromochloracetamide are formed.

The mother liquor obtained in the action of bromine on chloranilic and bromanilic acids contained, besides oxalic acid, chlorodibromomethane and bromoform respectively. N. H. M.

Galloflavin. By R. Bohn and C. Graebe (*Ber.*, **20**, 2327—2331). —*Galloflavin*, $C_{13}H_6O_9$ (?), is obtained by dissolving 50 grams of gallic acid in 875 c.c. of alcohol and 1 litre of water, cooling to $-5°$ to $+5°$, and adding 135 c.c. of 28 per cent. aqueous potash. Air is passed through for five hours. The potassium salt which separates is dissolved in hot water (at 90°), and treated with acid with exclusion of air. Galloflavin separates in greenish-yellow, crystalline plates. When heated, it carbonises without melting. It dissolves sparingly in water, alcohol, and ether; alkalis and alkaline carbonates dissolve it with yellow colour; sulphuric acid dissolves it unchanged. The *potassium salt*, $C_{13}H_4O_9K_2$, is a greenish-yellow, crystalline substance, very sparingly soluble in cold water, insoluble in alcohol; when boiled with water, free galloflavin is formed. Galloflavin yields coloured insoluble salts with the oxides of aluminium and chromium. The *acetyl-derivative*, $C_{13}H_2O_9Ac_4$, crystallises from benzene in white needles melting at 230°; it dissolves readily in glacial acetic acid and in chloroform, but is insoluble in alkaline carbonates. When galloflavin is heated with chloracetic chloride at 100—110° for 15 hours, the *compound* $C_{13}H_2O_9(CH_2Cl{\cdot}CO)_4$ is formed. This crystallises in white needles, soluble in ethyl acetate and acetic acid, very sparingly soluble in alcohol, ether, chloroform and benzene; it melts at 210—212°.

N. H. M.

Ethyl Parabromobenzoate and Parabromobenzoic Acid. By G. Errera (*Gazzetta*, **17**, 209—213).—According to the results described previously (p. 1103), ethyl parabromobenzyl ether is obtained by the action of alcoholic potash on parabromobenzyl chloride or bromide.

In a recent paper, Elbs (this vol., p. 151) has stated that ethyl parabromobenzoate is formed in the above reaction, together with parabromobenzyl alcohol and parabromobenzoic acid as subsidiary products; the view is supported by the formation of parabromobenzoic acid by the prolonged action of boiling alcoholic potash on the supposed ethereal salt.

To decide as to the correctness of Elbs' result, ethyl parabromobenzoate was prepared by the etherification of the corresponding acid; the compound obtained differs in boiling point (262°) from parabromobenzyl ethyl ether (243°), and is saponified immediately in the cold by alcoholic potash. The formation of parabromobenzoic acid from the ether is due to oxidation.

As a further point of difference, it is noted that parabromobenzyl ethyl ether on nitration forms parabromobenzaldehyde, whilst ethyl parabromobenzoate under the same conditions yields ethyl nitrobromobenzoate, $COH_3Br(NO_2)\cdot COOEt$ [COOEt : NO_2 : Br = 1 : 3 : 4].

In conclusion, some details are given as to the best method of preparing parabromobenzoic acid by the oxidation of the corresponding bromotoluene. V. H. V.

Derivatives of Phenylamidoacetic Acid. By O. Rebuffat (*Gazzetta*, **17**, 231—236).—*Acetylphenylamidoacetic acid*,

$$NPhAc\cdot CH_2\cdot COOH,$$

obtained by heating phenylamidoacetic acid with acetic anhydride in presence of benzene, crystallises in micaceous laminæ, melting at 190—191°, very soluble in water and alcohol, sparingly soluble in benzene.

Benzoylphenylamidoacetic acid, $NPhBz\cdot CH_2\cdot COOH$, is prepared in like manner to the above, and may be purified by means of its sodium salt, which crystallises on slow evaporation in large, tabular crystals. The acid is a white, amorphous precipitate, melting at 63°; the *copper* salt is an amorphous, green precipitate.

In the course of the preparation of phenylamidoacetic acid from aniline and monochloracetic acid, the formation of a black, resinous substance is observed, the quantity of which increases with the quantity of water in excess of a certain proportion, and the time employed in evaporating the solution for crystallising the amido-acid. Thus if one molecular proportion of monochloracetic acid and two of aniline are heated together, this black resin is the sole product. If this substance is purified from the accompanying aniline hydrochloride and phenylamidoacetanilide residue, dissolved in hydrochloric acid, and then reprecipitated with water, an acid is obtained crystallising in micaceous scales which decompose at 190—195°. Analysis points to *phenylglycinephenylamidoacetic acid*,

$$NHPh\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot COOH.$$

When impure, the acid rapidly turns black; it is sparingly soluble in water, but soluble in alcohol; it readily decomposes carbonates. V. H. V.

Derivatives of Hydrothiocinnamic Acid. By S. Bondzynski (*Monatsh. Chem.*, **8**, 349—364; compare Abstr., 1886, 325).—*Hydrothiocinnamic acid*, $CHPh : C(SH)\cdot COOH$, obtained by heating "benzylidene-rhodanic acid," $C_6H_5\cdot CH : C(SH)\cdot CO\cdot SCN$, with baryta-water, forms a yellowish, crystalline powder, and melts at 119°. It is easily soluble in alcohol, ether, benzene, &c., almost insoluble in water. The alkaline salts are easily soluble in alcohol and water, the salts of the

heavy metals are insoluble. When treated with iodine in carbon bisulphide solution, *bisulphid-cinnamic acid*,

$$CHPh:C(COOH)\cdot S\cdot S\cdot C(COOH):CHPh,$$

is obtained; this crystallises in slender, yellow needles melting at 179°. The *sodium* salt of this acid is an orange-yellow, amorphous substance easily soluble in water, quite insoluble in alcohol. The *potassium* salt is soluble in both alcohol and water. The *barium* and *magnesium* salts are easily soluble in water; the salts of the heavy metals are quite insoluble in water. Bromine acts on hydrothiocinnamic acid in the same manner as iodine. Hydriodic and hydrobromic acids do not combine with the acid.

When benzylidene-rhodanic acid is treated with a mixture of nitric and sulphuric acids, a violent action takes place, and two substances are obtained, one readily soluble in alcohol, the other sparingly soluble. The former, which crystallises in bright-yellow, rhombic prisms, is *nitrohydrothiocinnamic acid;* when purified by means of the barium salt and recrystallised from alcohol, it melts at 240°. The second, nearly insoluble substance appears to be a *nitrobenzylidene-rhodanic acid;* it melts at 263—265°. This method, however, does not give a good yield; the author therefore prepares *orthonitrohydrothiocinnamic acid* by heating together in alcoholic solution orthonitrobenzaldehyde and thiocyanic acid. The resulting orthonitrobenzylidene-rhodanic acid is a white, crystalline powder, insoluble in water, soluble in alcohol; it melts at 188—189°. When this substance is treated with baryta-water, an acid barium salt of the acid is obtained in orange crystals; it is therefore necessary to saponify the acid by heating it with excess of crystallised barium hydroxide.

When the nitro-compound is reduced with alcoholic ammonium sulphide, a small quantity of *amidohydrothiocinnamic acid* is formed. When reduced with ferrous sulphate, it yields *orthamidobenzylidene-rhodanic acid*, $C_6H_4(NH_2)\cdot CH:C(SH)\cdot CO,SCN$; this forms brilliant, blood-red crystals, which are completely decomposed on heating at 265—269°. The substance still retains acid properties; it is soluble in alkalis and reprecipitated by dilute acids. When heated with acetic anhydride, it gives the *diacetate*, which crystallises in yellow needles and melts at 189°. A little *monacetate* is also produced; this forms long, citron-yellow needles melting at 280—285°. Attempts to obtain orthohydrothiocinnamic acid from orthamidobenzylidene-rhodanic acid by treatment with baryta were unsuccessful, as also were endeavours to diazotise the latter substance. G. H. M.

Paracoumaric Acid. By G. Eigel (*Ber.*, **20**, 2527—2539).—Paracoumaric acid was prepared by the three known methods: from aloes (*Annalen*, **136**, 31), from parahydroxybenzaldehyde (this Journal, 1877, ii, 893), and from paradiazocinnamic acid, and modifications are described by which the yield may be much increased. Methyl-paracoumaric acid was also prepared by Perkin's reaction from anis-aldehyde (Abstr., 1877, i, 40), and by the methylation of paracoumaric acid. A comparison of these acids with naringenic and methylnaringenic acids respectively establishes their identity (this vol., p. 497).

Hydromethylnaringenic acid, formed by the reduction of methylnaringenic acid with sodium, is identical with hydromethylparacoumaric acid; it crystallises in feather-like forms, but after conversion into the sodium salt and treatment with an acid is obtained in long, colourless needles; the crystals of both forms are anhydrous. The *silver* salt, $C_{10}H_{11}AgO_3$, crystallises in small needles, is sparingly soluble in hot water, and when dry is unaffected by light; the *barium* salt, $(C_{10}H_{11}O_3)_2Ba + 2H_2O$, crystallises in cubic forms. The *methyl* salt, $C_{11}H_{14}O_3$, obtained in small quantity only by saturating a solution of the acid in methyl alcohol with hydrogen chloride, is readily prepared by heating the acid (1 mol.), with potassium hydroxide (2 mols.), methyl iodide (2 mols.), and some methyl alcohol at 140° for an hour; it boils at 265—270°, solidifies at 0° to a crystalline mass which melts at 38°, and is identical with methyl hydromethylparacoumarate.

When dry paracoumaric acid in ethereal solution is treated with bromine (1 mol.), and the solvent is removed by evaporation in a current of air, colourless crystals of what is perhaps a paracoumaric acid dibromide are obtained; these melt at 97—101° and decompose on drying. *Bromoparacoumaric acid dibromide*,

$$OH\cdot C_6H_3Br\cdot CHBr\cdot CHBr\cdot COOH,$$

is formed when paracoumaric acid dissolved in acetic acid or absolute ether is treated with an excess of bromine; it crystallises from chloroform in needles and melts at 188°. On treatment with alcoholic potash, it yields *bromoparavinylphenol dibromide*,

$$OH\cdot C_6H_3Br\cdot CHBr\cdot CH_2Br.$$

This compound is crystalline, melts at 108°, and yields an *acetyl*-derivative, $C_6H_6Br_3OAc$, melting at 94°.

Methylparacoumaric acid dibromide, $OMe\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COOH$, is prepared by the action of bromine on methylparacoumaric acid in equimolecular proportions; chloroform is used as a solvent, and must be removed by evaporation at the ordinary temperature. It forms colourless crystals, which melt at 149° when heated rapidly, and at 168° when slowly heated; heat readily decomposes it. The *methyl* salt has been already described (this vol., p. 488); when treated with alcoholic potash, it yields two acids crystallising in needles, one of which is soluble in hot water, and melts at 158—168°, whilst the second is soluble in hot alcohol, and melts at 127—132°. If methylparacoumaric acid dibromide is heated with aqueous potash, *bromoparavinylanisoïl*, $OMe\cdot C_6H_4\cdot CH:CHBr$, is obtained; this crystallises from alcohol in scales, melts at 54·5°, is volatile with steam, and has an odour and taste resembling that of anise and fennel.

On treatment with an excess of bromine in chloroform solution, methylparacoumaric acid yields *bromomethylparacoumaric acid dibromide*, $OMe\cdot C_6H_3Br\cdot CHBr\cdot CHBr\cdot COOH$, which crystallises from ether or chloroform in needles, melts at 162°, and is decomposed by alcohol and water. When heated with 30 per cent. aqueous potash, it is converted into *bromoparacetyleneanisoïl*, $OMe\cdot C_6H_3Br\cdot C:CH$. This compound crystallises from alcohol in scales, melts at 75°, is volatile with steam, and yields a greenish-yellow, feebly explosive precipitate with ammoniacal cuprous chloride solution. W. P. W.

Homo-orthophthalimide. By G. Pulvermacher (*Ber.*, **20**, 2492—2499; compare this vol., pp. 50, 725).—When a solution of homo-orthophthalimide (1 mol.) and sodium (2 mols.) in alcohol is digested with ethyl iodide (2 mols.) at 100°, *α-diethylhomo-orthophthalimide*, $C_9H_5Et_2NO_2$, is obtained; this crystallises from alcohol in white scales, melts at 144°, and is soluble in alkalis. By the further action of ethyl iodide and alcoholic potash on this compound at 100°, *triethylhomo-orthophthalimide*, $C_9H_4Et_3NO_2$, is formed; this is a glistening, white, crystalline mass, which melts at 50°, and is extremely soluble in all ordinary solvents, but is insoluble in alkalis.

Homo-orthophthalethylimide, $C_6H_4<\begin{matrix}CH_2\cdot CO\\CO\cdot NEt\end{matrix}>$, is prepared by distilling a solution of homo-orthophthalic acid in ethylamine. It crystallises in yellowish needles, melts at 105°, and is readily soluble in all ordinary solvents and in alkalis. When ethylated, it yields triethylhomo-orthophthalimide, whose constitution therefore is probably represented by the formula $C_6H_4<\begin{matrix}CEt_2\cdot CO\\CO\cdot NEt\end{matrix}>$. Diazobenzene chloride and benzaldehyde react with the ethylimide, and form compounds analogous to those obtained by the action of these substances on homo-orthophthalimide (*loc. cit.*); *homo-orthophthalethylimidazobenzene*, $C_{11}H_{10}NO_2\cdot N_2Ph$, crystallises from alcohol in yellow needles melting at 139°, and *benzalhomo-orthophthalethylimide*,

$$Ph\cdot CH : C_{11}H_9NO_2,$$

crystallises from acetic acid in stellate groups of yellow needles, melting at 97°.

α-Diethylhomo-orthophthalic anhydride, $C_9H_4Et_2O_3$, is obtained when diethylhomo-orthophthalimide is heated with fuming hydrochloric acid at 230°. It crystallises in colourless scales, melts at 53°, and is sparingly soluble in ammonia, but soluble in warm aqueous alkalis. The *barium* salt, $C_9H_4Et_2O_4Ba$, crystallises in white, silky scales; the *silver* salt, $C_9H_4Et_2O_4Ag_2$, was also prepared. When mixed with soda-lime and distilled over lime, the anhydride yields a red oil, from which diethyltoluene, $C_6H_5\cdot CHEt_2$ (b. p. = 178°), can be separated by fractionating between 170—180°. If the solution of the anhydride in aqueous potash is treated in the cold with hydrochloric acid, *α-diethylhomo-orthophthalic acid*, $COOH\cdot C_6H_4\cdot CEt_2\cdot COOH$, separates as a crystalline precipitate, which after crystallisation from alcohol, melts at 148° and is converted into the anhydride.

α-Dibenzylhomo-orthophthalimide, $C_9H_5(C_7H_7)_2NO_2$, obtained by digesting homo-orthophthalimide with sodium and benzyl chloride in alcoholic solution, crystallises in yellow scales and melts at 174°. Unlike the diethylimide, it is insoluble in alkalis, and is only attacked by hydrochloric acid with difficulty even at 300°, when it yields a compound which seems to be the *anhydride* of α-dibenzylhomo-orthophthalic acid; this crystallises in yellow needles, melts at 191°, and is sparingly soluble in alkalis.

Homo-orthophthalbenzylimide, $C_{16}H_{13}NO_2$, obtained by distilling homo-orthophthalimide with benzylamine, forms yellowish-green crystals which melt at 127°, and are soluble in alkalis. When heated with

benzyl chloride and an alkali, it yields *α-dibenzylhomo-orthophthalbenzylimide* (tribenzylhomo-orthophthalimide), $C_9H_4(C_7H_7)_3NO_2$, identical with that prepared in a similar manner from dibenzylhomo-orthophthalimide; this crystallises in yellowish-white scales, and melts at 109°. W. P. W.

Homo-orthophthalimide and the Homologues of Isoquinoline. By S. Gabriel (*Ber.*, **20**, 2499—2506).—*Ethyl homo-orthophthalate*, $COOEt\cdot C_6H_4\cdot CH_2\cdot COOEt$, is obtained either by treating the silver salt of the acid with ethyl iodide, or by saturating an alcoholic solution of the acid with hydrogen chloride. It is a thick oil with a faint, aromatic odour, boils at 291·5—292·5°, and is not acted on when treated with sodium in alcoholic solution and then digested with ethyl iodide.

α-Methylhomo-orthophthalonitrile, $CN\cdot C_6H_4\cdot CHMe\cdot CN$, is prepared by treating a lukewarm alcoholic solution of orthocyanobenzyl cyanide (5·7 grams) with methyl iodide (3 c.c.) and an alcoholic solution of potassium hydroxide (2·25 grams), cooling the mixture when necessary, and finally heating at 100° to complete the reaction; the residue left on distilling off the alcohol is then treated with water, extracted with ether, and the oil remaining after the evaporation of the ether is purified by distillation. It crystallises in large triclinic forms, $a : b : c = 0{\cdot}9449 : 1 : 1{\cdot}0809$; $\alpha = 97°\ 2'$; $\beta = 103°\ 12'$; $\gamma = 87°\ 11'$; melts at 36—37°, boils at 284—286°, is only slightly volatile with steam, and is readily soluble in the ordinary solvents, sparingly soluble in light petroleum. When the nitrile is dissolved in sulphuric acid, heated at 100° until the reaction is complete, and the product poured into water—

α-Methylhomo-orthophthalimide, $C_6H_4{<}\begin{matrix}CHMe\cdot CO\\ CO\text{—}NH\end{matrix}{>}$, is obtained; this crystallises in compact, glistening prisms, melts at 145°, distils without decomposition, and dissolves in alkalis. On digestion with methyl iodide and alcoholic potash, this compound is converted into trimethylhomo-orthophthalimide (this vol., p. 50). When the methylimide is heated with fuming hydrochloric acid at 190—200° for two hours, it yields *α-methylhomo-orthophthalic acid;* this is a crystalline powder, which melts at 146—147° and dissolves in ammonia and alkalis. The *silver* salt, $C_{10}H_8Ag_2O_4$, was analysed.

Methyldichlorisoquinoline, $C_6H_4{<}\begin{matrix}CMe : CCl\\ CCl : N\end{matrix}{>}$, is prepared by heating α-methylhomo-orthophthalimide (5 grams) with phosphorus oxychloride (15 c.c.) at 190—200° for four hours, extracting the product with water, and heating the crystalline residue with very dilute aqueous soda; the insoluble methyldichlorisoquinoline is then purified by distillation and crystallised from alcohol. It crystallises in long, white needles, and melts at 101—102°. On treating the alkaline filtrate with an acid, it yields *methylchloroxyisoquinoline*, $C_6H_4{<}\begin{matrix}CMe : C(OH)\\ CCl : N\end{matrix}{>}$ or $C_6H_4{<}\begin{matrix}CHMe\cdot CO\\ CCl : N\end{matrix}{>}$, which crystallises from acetic acid in needles, and melts at 224° with frothing.

Homo-orthophthalonitrile, when ethylated under conditions similar

to those detailed for the methyl-derivative, yields *α-ethylhomo-orthophthalonitrile*, $CN{\cdot}C_6H_4{\cdot}CHEt{\cdot}CN$, which crystallises in short, compact prisms, melts at 39—40°, and distils at 293—295°. On treatment with sulphuric acid, the ethyl nitrile is converted into *α-ethylhomo-orthophthalimide*, $C_{11}H_{11}NO_2$; this crystallises in colourless needles, melts at 97—99°, dissolves in alkalis, and when heated with phosphorus oxychloride yields *ethyldichlorisoquinoline*,

$$C_6H_4\begin{matrix}<CEt:CCl\\ -CCl:N-\end{matrix}>.$$

Orthocyanobenzyl cyanide, when heated at 80° with concentrated sulphuric acid, or at 100° with fuming hydrochloric acid, is converted into homo-orthophthalimide. W. P. W.

Transformation of Homologues of Indole into those of Quinoline. By G. Magnanini (*Gazzetta*, **17**, 246—254).—Though indole and pyrroline are regarded as possessing an analogous constitution, yet this view has not as yet been confirmed by experimental evidence. Ciamician and Dennstedt have shown that derivatives of pyrroline are readily converted by chloroform or bromoform into those of pyridine; by the same reaction, derivatives of indole should be converted into those of quinoline. In this paper, it is shown that methylketole and skatole yield substances which are in all probability halogen-derivatives of quinoline. For example, methylketole when heated with chloroform in presence of alcoholic soda is converted by a violent reaction into a chloroquinaldine thus: $C_9H_9N + 2NaOH + CHCl_3 = C_{10}H_8ClN + 2NaCl + 2H_2O$; the product is best purified by means of the picrate, and subsequent decomposition of the salt formed by potash.

Chloroquinaldine, C_9H_5NMeCl, crystallises in delicate, white needles, melting at 71—72°, insoluble in water, very soluble in alcohol and ether; the *picrate* forms sparingly soluble, yellow needles melting at 223° with decomposition.

Bromoquinaldine, C_9H_5NMeBr, obtained from bromoform under identical conditions, crystallises in white needles melting at 78°: system, monoclinic; $a : b : c = 0{\cdot}91 : 1 : 0{\cdot}624$; $\beta = 64° 31' 33''$. The *picrate* melts at 224—225°.

In like manner, skatole yields a *chloro-* and *bromo-lepidine;* the former crystallises in delicate needles melting at 54—55°, and the picrate melts at 208°; the latter melts at 58·5—59·5°, and its picrate at 214—215° with decomposition.

The above derivatives are not identical with the methyl halogen-derivatives previously described; the author considers that the chloroquinaldine from methylketole has the constitution Me : Cl = 2′ : 3′, while the chlorolepidine from skatole has the constitution Cl : Me = 3′ : 4′. V. H. V.

Chlorobromonaphthalene. By J. Guareschi and P. Biginelli (*Chem. Centr.*, 1887, 518—519).—By the action of bromine (1 mol.) on α-monochloronaphthalene (1 mol.), and by the action of chlorine on α-monobromonaphthalene, the same dihalogen-naphthalenes are

obtained; in both cases two chlorobromonaphthalenes, $C_{10}H_6ClBr$, melting at 66—67° and at 119—119·5° are formed. *Parachlorobromonaphthalene* melts at 66—67°, boils at 303° (uncorr.), dissolves in ether and acetic acid, and sublimes in needles; when oxidised with chromic acid (two parts) in acetic acid solution, chlorobromonaphthaquinone and parachlorobromophthalide are formed. The quinone (probably *parachlorobromo-α-naphthaquinone*) crystallises from alcohol in yellow needles of a silky lustre melting at 166·5—167°. *Parachlorobromophthalide* crystallises in tabular, rhombohedral crystals melting at 179·5—180°.

The derivative melting at 119—119·5° forms thin, lustrous plates, more sparingly soluble in alcohol and glacial acetic acid than its isomeride; when oxidised with chromic acid, α-chlorophthalic acid, melting at 183—184°, is formed (Guareschi, Abstr., 1886, 353). In the compound melting at 119°, the halogen is therefore contained in both benzene nuclei. N. H. M.

Nitrosamines. By O. Fischer and E. Hepp (*Ber.*, **20**, 2471—2478).—When an alcoholic solution of β-naphthylethylnitrosamine, cooled in ice, is treated with alcoholic hydrogen chloride, *α-nitroso-β-ethylnaphthylamine*, [NO : NHEt = 1 : 2], is obtained; this crystallises from benzene in well-formed, flat tables, melts at 120—121°, and yields salts readily soluble in water. On the addition of potassium nitrite to the solution of the base in dilute sulphuric acid, a nitrosamine is formed, and crystallises in long, hair-like needles, whilst on reduction with tin and hydrochloric acid, or allowing a solution of the base in alcoholic hydrogen chloride to remain at 10—15° for some time, or on treating β-naphthylethylnitrosamine with alcoholic hydrogen chloride at the ordinary temperature, ethenyl-α-β-naphthylenediamine, $C_{12}H_{10}N_2$ (this vol., p. 729), is obtained. The *hydrochloride* of the anhydro-base, $C_{12}H_{10}N_2,HCl + 2H_2O$, crystallises in slender, colourless needles, and is sparingly soluble in water, and the base itself is identical with that prepared by Liebermann and Jacobson (Abstr., 1882, 521).

The base obtained from β-phenylnaphthylnitrosamine by treating its alcoholic solution in the cold with alcoholic hydrogen chloride, is identical with naphthaphenazine (this vol., p. 591); the yield amounts to 10 per cent.

Nitrosoaniline, $C_6H_6N_2O$, is formed when nitrosophenol (1 part) is heated with ammonium chloride (5 parts) and ammonium acetate (10 parts) at 100° for half an hour; the product is then poured into water, and the dark-green, crystalline precipitate is purified by crystallisation from benzene. It forms steel-blue, curved needles, and melts at 173—174°. Like nitrosodimethylaniline, it yields sodium nitrosophenol and ammonia, when boiled with aqueous soda. Although nitrosoaniline could not be obtained by the action of ammonia on nitrosophenol, it is possible to prepare α-nitroso-β-ethylnaphthylamine by heating α-nitrosonaphthol with ethylamine at 100°, and the authors suggest that Ilinski's orthonaphthalene-α-oxime-β-imide (Abstr., 1886, 474) should be regarded as α-nitroso-β-naphthylamine.

When nitrosophenylglycocine (Abstr., 1878, 795) is dissolved in 2 parts of alcohol, treated with 3 parts of alcoholic hydrogen chloride, and allowed to remain for 12 hours, a crystalline mass is obtained which is precipitated from cold alcoholic solution by ether in yellow scales of the composition $C_6H_6N_3OCl$. The compound explodes when heated, is decomposed by water with the evolution of two-thirds of its nitrogen, and dissolves in concentrated hydrochloric acid without decomposition. Its *platinochloride*, $(C_6H_6N_3OCl)_2,PtCl_4$, crystallises in yellow scales, and decomposes on boiling with water with a separation of platinum. The compound is regarded as the diazo-salt of phenylhydroxylamine, since the aqueous solution after boiling reduces silver and cupric salts, and the compound when added to boiling absolute alcohol decomposes with evolution of nitrogen and an odour of aldehyde, and after distilling off the alcohol it yields a residue from which a pale-yellow oil can be separated by steam distillation. The oil, $C_{12}H_{12}N_2O_2$, has all the properties of a feeble base, and forms a *hydrochloride* crystallising in white prisms. This compound also reduces an ammoniacal silver solution, slowly reduces Fehling's solution, and is wholly converted into benzidine on treatment with tin and hydrochloric acid. It is regarded as diphenyldihydroxylamine, $OH{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}OH$ [$NH{\cdot}OH : C_6H_4 = 1 : 4$].

W. P. W.

Derivatives of Camphor. By L. Balbiano (*Gazzetta*, **17**, 240—245).—It has recently been shown by the author (this vol., p. 1049) that the reaction of phenylhydrazine on camphor is essentially different from that of the same reagent on substances formed on the ethylenic oxide type, such as epichlorhydrin. In continuation of experiments on the derivatives of camphor, it is shown that chloro- and bromo-camphor, on oxidation with alkaline permanganate, yield camphoric acid, thus confirming the results of Armstrong (*Ber.*, **12**, 1358) and Schiff (*Gazzetta*, **9**, 324) in opposition to those of Cazeneuve. The inertness of derivatives of camphor towards hydroxylamine affords no evidence as to the absence of the carbonyl-group in these compounds, inasmuch as the reaction will not proceed in the presence of solvents, and even phenylhydrazine under these conditions will not always react, and, secondly, some compounds containing two carbonyl-groups, such as benzoylacetone and phenanthraquinone, react only with partial substitution of the isonitroso-residue.

V. H. V.

Strophanthin. By T. R. Fraser (*Pharm. J. Trans.* [3], **18**, 69).—It has been found that the substance obtained by the former process for the preparation of strophanthin, is resolved by lead acetate into at least two others—one an extremely active glucoside, and the other an acid for which the name *kombic acid* is suggested. To obtain pure strophanthin, the following is the process ultimately adopted. The product obtained in the earlier process is dissolved in water, tannic acid is added, and the tannate digested with recently precipitated lead oxide. The alcoholic extract from this is precipitated with ether, the precipitate dissolved in weak alcohol, and carbonic anhydride is passed through the liquid for several hours to remove lead. The solution is then evaporated at a low temperature and dried in a

vacuum. Strophanthin thus obtained is imperfectly crystalline, neutral, intensely bitter, freely soluble in water, less so in rectified spirit, and nearly insoluble in ether and chloroform. It burns without residue, and the results of analysis agree fairly with the formula $C_{20}H_{34}O_{10}$. Nearly all acid reagents cause its solutions to become turbid, and the liquid is then found to contain glucose. This decomposition is also produced by hydrogen sulphide, especially when heated. Many organic acids, and all mineral acids, except carbonic, resolve strophanthin, even in the cold, into glucose and a substance which the author names *strophanthidin*. Therefore, neither hydrogen sulphide nor acids (especially mineral acids) should be used in the preparation of strophanthin. The crystalline product obtained by Hardy and Gallois in 1877, by extracting the seeds with rectified spirit acidified with hydrochloric acid, was supposed by them to be strophanthin; and as it failed to yield glucose when heated with dilute sulphuric acid, they inferred that strophanthin is not a glucoside. But there can be little doubt, both from the mode of its preparation and also from its reactions, that their product was strophanthidin. R. R.

Strophanthus and Strophanthin. By E. Merk (*Pharm. J. Trans.* [3], **18**, 72).—When the fatty oil in the seeds of Strophanthus is extracted by ether previously to treating them with alcohol, the ethereal solution will also contain a certain amount of strophanthin, and to this circumstance the small activity of the alcoholic tincture of strophanthus of commerce is in part due. The author obtains strophanthin as a white, crystalline powder which melts at 185° and volatilises without residue. R. R.

Strophanthus and Strophanthin. By W. Elborne (*Pharm. J. Trans.* [3], **18**, 219).—The following process for preparing strophanthin obviates certain objections to which Gerrard's process is open. The seed in fine powder is mixed into a thin paste with water to which 10 per cent. of alcohol has been added; this is set aside for 12 hours, then agitated with six times its volume of absolute alcohol, and, after six hours, is filtered. The residue is washed with rectified spirit, and the washings added to the filtrate, and from the whole four-fifths of the alcohol is removed by distillation. To the remainder, solution of lead subacetate is added, and the mixture is heated to 100°, filtered, and allowed to cool. The lead is then removed from the cold filtrate by precipitation with hydrogen sulphide; the filtrate is agitated with amyl alcohol, which dissolves out the strophanthin and yields it on evaporation as a colourless film that crumbles on removal into a non-deliquescent, white powder. R. R.

Chlorophyll. By A. Tschirch (*Chem. Centr.*, 1887, 669).—Phyllocyanic acid is obtained by dissolving crude chlorophyllan in concentrated hydrochloric acid, and precipitating with excess of water. This substance can also be obtained in minute crystals from solutions in alcohol and ether. Its spectrum agrees with that of chlorophyllan; it also gives a zinc compound containing 11·07 per cent. of the metal; with alkalis it forms very soluble combinations. The formula

$C_{28}H_{47}N_2O_6$ is provisionally assigned to this compound. The proportion of phyllocyanic acid present, which appears in leaves in the form of chlorophyll, can be estimated by the chemical or spectroscopical methods. In the dark-brown leaves of the *Fuchsia ovata*, the proportion of the absorbing chlorophyll matter varied from 2·5 to 5 per cent. of the dried substance, apart from the ash of the leaves; the presence of copper diminishes the fluorescence. V. H. V.

Preparation of Picrocarmine. By L. Gedölst (*Chem. Centr.*, 1887, 599).—In order to prepare picrocarmin for microscopical purposes the following method is proposed. About half a gram of carmine is dissolved in 100 c.c. of water containing 5 c.c. of a 1 per cent. solution of soda; the solution is then boiled, filtered, and made up again to 100 c.c. To neutralise the liquid, it is mixed with an equal volume of water; a 1 per cent. solution of picric acid is then added, which causes at first a turbidity which subsequently disappears; the non-disappearance of the turbidity serves as an indication that the point of neutralisation has been passed. V. H. V.

Diastase. By L. Schärtler (*Chem. Centr.*, 1887, 534).—Pure diastase is prepared as follows:—10 kilos. of light, ground malt, 50 grams of sodium hydrogen carbonate, and 12 to 14 litres of water are heated at 40°, digested for two hours, the liquid drawn off, and 6 to 8 litres more water added. After some time, the second supply of water is drawn off, added to the first liquor, heated at 65°, and passed through a sieve; twice the volume of alcohol is added and the clear solution drawn off; the residue containing the diastase is treated with a little warm distilled water, the solution separated from the undissolved albuminoïds, and precipitated with alcohol. It is dried at 50° and then powdered. The yield is 1 to $1\frac{1}{2}$ per cent. N. H. M.

Pyridinepolycarboxylic Acids. By J. Weber (*Annalen*, **241**, 1—32).—Carbodinicotinic acid, or 2:3:5-pyridinetricarboxylic acid, cannot be obtained directly from pyridinetetracarboxylic acid, but it can be prepared by starting from symmetrical lutidinedicarboxylic acid. On oxidation with the theoretical quantity of potassium permanganate, *α-methylcarbodinicotinic acid* (2:3:5 α-picolinetricarboxylic acid), $C_5NHMe(COOH)_3$, is formed. It is isolated by acidifying the crude product with acetic acid and adding barium chloride. The precipitate is washed and decomposed by a slight excess of dilute sulphuric acid. On evaporating the filtrate, α-methylcarbodinicotinic acid is deposited in crystalline masses. The acid crystallises with 1 mol. H_2O. It turns yellow at 170°, and melts with decomposition at 226°, forming a crystalline sublimate; if kept at a temperature of 150° for some time, it is converted into α-methyldinicotinic acid. The free acid forms precipitates in solutions of silver, lead, mercurous, cadmium, and zinc salts, also with barium and calcium salts in the presence of ammonia. The copper and silver salts, and the acid potassium salt, $C_5NHMe(COOH)_3 + C_5NHMe(COOH)_2{\cdot}COOK + 6H_2O$, are crystalline.

α-Methyldinicotinic acid, $C_5NH_2Me(COOH)_2 + H_2O$ [Me : $(COOH)_2$

= 2 : 3 : 5], is soluble in hot water, and is deposited on slowly cooling the solution in needle-shaped crystals. The acid melts between 245° and 250° with decomposition. The neutral solution gives crystalline precipitates with lead ($C_8H_5NO_4Pb + 2H_2O$) and cadmium salts, and amorphous precipitates with the salts of silver and mercury.

The *hydrochloride*, $C_8H_7NO_4,HCl + 1$ or $1\frac{1}{2}H_2O$, forms transparent crystals which rapidly become opaque on exposure to the air.

Carbodinicotinic acid, $C_5NH_2(COOH)_3 + 1\frac{1}{2}H_2O$, is formed by the oxidation of the preceding acid with potassium permanganate. Nitrate of silver is added to the crude solution, the precipitate is dissolved in the minimum quantity of boiling nitric acid, and on cooling, the acid silver salt crystallises out. The free acid is liberated by the action of hydrogen sulphide on the silver salt. It dissolves freely in hot water, and forms colourless crystals. Prolonged heating at 150° completely converts the acid into dinicotinic acid which melts at 323° with decomposition.

β-Carbocinchomeronic acid (3 : 4 : 5-pyridinetricarboxylic acid), $C_5NH_2(COOH)_3 + 3H_2O$, can be prepared by converting 4-phenylpyridinetetracarboxylic acid into 4-phenyldinicotinic acid and oxidising the phenyl in this acid to carboxyl. A much better yield is obtained by heating pyridinepentacarboxylic acid or its acid potassium salt, $C_5N(COOH)_3(COOK)_2 + 3\frac{1}{2}H_2O$. The crude product is converted into the silver salt, which is decomposed by hydrochloric acid yielding a mixture of cinchomeronic and β-carbocinchomeronic acids. The former is sparingly soluble in water. β-Carbocinchomeronic acid crystallises in plates and melts with decomposition at 261°. The silver salt, $C_5NH_2(COOAg)_3 + 2H_2O$, and the calcium and barium salts are crystalline.

Berberonic acid is neither identical with β-carbocinchomeronic acid nor with carbodinicotinic acid. It must therefore be regarded as α′-carbocinchomeronic acid.

Symmetrical and unsymmetrical pyridinetetracarboxylic acids have been prepared, but not the "consecutive" isomeride 2 : 3 : 4 : 5-pyridinetetracarboxylic acid. Lutidinetricarboxylic acid is converted into 2 : 4-dimethyldinicotinic acid [$Me_2 : (COOH)_2 = 2 : 4 : 3 : 5$] at 175°; this crystallises in yellow needles containing 2 mols. H_2O. The acid loses its water of crystallisation at 130° and melts at 255° with decomposition. The *hydrochloride* crystallises with 1 or $\frac{1}{2}$ mol. H_2O. The *platinochloride*, $(C_9NH_9O_4)_2,H_2PtCl_6$, forms orange-coloured plates, and is decomposed by water. On oxidation with potassium permanganate, 2 : 4-dimethyldinicotinic acid yields a mixture of pyridinetetracarboxylic and 4-methylcarbodinicotinic acids. The tetracarboxylic acid [$(COOH)_4 = 2 : 3 : 4 : 5$] crystallises in prisms containing 2 or 3 mols. H_2O. At 120° it begins to lose carbonic anhydride, yielding β-carbocinchomeronic acid. The *barium* salt, $C_9NHO_8Ba_2 + 4H_2O$, is precipitated on adding barium chloride to a solution of ammonium pyridinetetracarboxylate. The *acid silver* salt,

$$C_5NH(COOH)(COOAg)_3 + C_5NH(COOAg)_4 + 1H_2O,$$

is precipitated on the addition of silver nitrate to the acid in the presence of a small quantity of nitric acid.

4-*Methylcarbodinicotinic acid* or 2:3:5-*picolinetricarboxylic acid*, [Me : $(COOH)_3 = 4:2:3:5$], is less soluble in water than the tetracarboxylic acid. It crystallises with 1 mol. H_2O in needles and with 2 mols. H_2O in prisms. When the acid is heated at 205°, it turns yellow and slowly loses carbonic anhydride, forming a black porous mass; at 258—260° a rapid evolution of gas takes place, and the mass swells up to three or four times its original volume. The free acid produces in silver, lead, copper, and mercurous salts precipitates which become crystalline after a time. In presence of ammonia, the acid gives crystalline precipitates with calcium and barium salts. In hot solutions, cadmium sulphate produces a crystalline precipitate which redissolves on cooling. Ferrous sulphate gives rise to a deep-red coloration. The constitution of the acid is verified by the fact that the calcium salt on dry distillation yields the γ-picoline described by Lange (Abstr., 1886, 256). W. C. W.

New Dimethoxyquinoline. By G. Goldschmiedt (*Monatsh. Chem.*, **8**, 342—348).—In the course of experiments made to ascertain the position of the methoxy-groups in papaverine, the author prepared a dimethoxyquinoline from the nitro-compound of veratric acid, $COOH{\cdot}C_6H_3(OMe)_2 = (1:3:4)$, by reducing this with tin and hydrochloric acid, and directly condensing the stannochloride of amidoveratric acid with glycerol, according to Skraup's method.

The dimethoxyquinoline so obtained was an oil, the boiling point of which was not determined. The *hydrochloride* obtained by dissolving the base in dilute hydrochloric acid forms large, white needles, easily soluble in water, sparingly in alcohol. The *platinochloride* is a bright yellow, crystalline powder. The *picrate* is obtained in slender, yellow needles, which melt at 257° with violent decomposition. The *chromate* consists of a bright yellow, crystalline powder.

The position of the nitrogen to the methoxy-groups in this compound is not certain, since the position of the nitro-group in the nitroveratric acid is not definitely known, but the most probable position is [OMe : OMe : $NO_2 = 2:3:4$]. G. H. M.

Synthesis of Hydroxyquinolinecarboxylic Acid. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **8**, 311—326).—The preparation and properties of this acid have been previously described (this vol., p. 63); the authors, however, find that a larger yield is obtained when a smaller quantity of potassium hydroxide is used than was previously recommended. The pyridinedicarboxylic acid obtained by oxidation with alkaline permanganate has now been identified with Hoogewerff and van Dorp's quinolinic acid, since when heated it loses carbonic anhydride, and is converted into nicotinic acid. This acid must therefore be orthohydroxyquinolinecarboxylic acid. When brominated, the acid yields dibromhydroxyquinoline.

When *o*-hydroxyquinolinecarboxylic acid is treated with nascent hydrogen in acid solution, it yields *tetrahydrohydroxyquinolinecarboxylic acid*. This forms brilliant, quadratic crystals, which melt at 265° with decomposition; it is sparingly soluble in water and alcohol,

insoluble in benzene, ether, or chloroform. The aqueous solution has an acid reaction, reduces silver nitrate, and gives precipitates with salts of the heavy metals. Iron salts give a characteristic cherry-red coloration with the acid solution. Dilute nitric acid gives the nitrate, which forms brownish-yellow needles.

The *sulphate* and *acetate* are sparingly soluble in water. The *nitroso*-compound forms a white crystalline precipitate melting at 195°, which is slightly soluble in water or dilute acid, with a cherry-red coloration. When treated with ethyl iodide and alcohol, the tetrahydro-acid gives the *hydriodide* of *ethyltrihydrohydroxyquinolinecarboxylic acid*, which forms large white needles, easily soluble in hot water, more sparingly in cold. *Ethyltrihydrohydroxyquinolinecarboxylic acid* is obtained in beautiful prisms, when the hydriodide is decomposed with ammonia; it melts at 220°, and is very sparingly soluble in all solvents. Measurement of the crystals gave $a : b : c = 1 : 1{\cdot}510 : ?$.

Parahydroxyquinolinecarboxylic acid is obtained when parahydroxyquinoline, soda, and carbon tetrachloride are mixed in alcoholic solution, and the whole boiled for 2 to 3 hours. When purified, the acid separates as a white, flocculent precipitate, which melts at 220°, and gives a blood-red coloration with iron chloride. The *barium* salt forms slightly soluble, stellate prisms; the *copper*, *silver*, and *lead* salts are almost absolutely insoluble. The *hydrochloride* obtained by dissolving the acid in dilute hydrochloric acid is easily soluble in hot water, sparingly in cold; when dried over lime, it does not lose hydrochloric acid, thus differing from the analogous ortho-compound. The *platinochloride* is a dark-yellow, crystalline powder. Attempts to form a *hydro*-acid were unsuccessful. When oxidised with alkaline potassium permanganate, the acid yields quinolinic acid, so that this acid must also be regarded as a parahydroxyquinolinecarboxylic acid.

G. H. M.

Tetramethyldiquinolyline from Benzidine. By C. Schestopal (*Ber.*, **20**, 2506—2510).—*Tetramethyldiquinolyline*, $C_{22}H_{20}N_2$, is obtained by heating benzidine (1 mol.) with acetone (4 mols.) and concentrated hydrochloric acid at 180° for two days, and subsequently precipitating the base with an alkali; methane is formed during the reaction. A second method of preparation consists in saturating a mixture of acetone and paraldehyde in molecular proportions with hydrogen chloride, and after some hours heating the product with benzidine and concentrated hydrochloric acid in a reflux apparatus. The base crystallises in nacreous scales, melts at 232°, and is insoluble in water, sparingly soluble in ether, and readily soluble in alcohol. The *hydrochloride*, $C_{22}H_{20}N_2,2HCl$, crystallises in white, glistening needles, and is readily soluble in water, sparingly soluble in alcohol; the *sulphate*, $C_{22}H_{20}N_2,H_2SO_4$, crystallises from water in small, white needles, and from alcohol in large, rhombic prisms; the *dichromate*, $C_{22}H_{20}N_2,H_2Cr_2O_7$, crystallises in small, orange-yellow needles, which become brown on exposure to light, and are sparingly soluble in water; the *platinochloride*, $C_{22}H_{20}N_2,H_2PtCl_6$, crystallises in flat, reddish-yellow needles, and the *picrate* is insoluble in water and cold alcohol. The *methiodide*, $C_{22}H_{20}N_2,2MeI$, crystallises in yellow needles, melts at about 270° with decomposition, and is readily soluble in water and alcohol,

insoluble in ether; the *ethiodide*, $C_{22}H_{20}N_2,2EtI$, crystallises in large, flat, straw-coloured needles, melts at 158° with decomposition, and is soluble in alcohol and water, insoluble in ether; the hydrochloride of the *chloriodide*, $C_{22}H_{20}N_2,2ICl,2HCl$, forms slender, flesh-coloured needles. When the base is heated with benzaldehyde in the presence of zinc chloride at 180° for 4 to 5 hours, a compound is obtained, which crystallises from alcohol in large, yellow needles. The constitution of this tetramethyldiquinolyline is probably represented by the formula $<\begin{matrix}CH:CMe\\CMe:N\end{matrix}>C_6H_3\cdot C_6H_3<\begin{matrix}CMe:CH\\N:CMe\end{matrix}>$. W. P. W.

Pyrazolone-derivatives from Ethyl Benzoylacetate. By L. Knorr and C. Klotz (*Ber.*, **20**, 2545—2550).—Ethyl benzoylacetate, like ethyl acetoacetate, reacts with phenylhydrazine, and yields diphenylpyrazolone, and inasmuch as ethyl succinosuccinate (Abstr., 1884, 1380) and ethyl oxalacetate (this vol., p. 234) also form pyrazolone-derivatives under similar conditions, this reaction seems to be characteristic for ethyl salts of ketonic acids of the general formula $R\cdot CO\cdot CH_2\cdot COOEt$.

Diphenylpyrazolone, $NPh<\begin{matrix}CO\cdot CH_2\\N:CPh\end{matrix}>$, obtained by the action of phenylhydrazine on ethyl benzoylacetate, melts at 137°, and is very sparingly soluble in water, sparingly soluble in ether and light petroleum, readily soluble in alcohol, chloroform, benzene, and acetic acid. The *hydrochloride*, $C_{15}H_{12}N_2O,HCl$, crystallises in small, white needles, and is readily soluble in alcohol; the *sulphate*, $C_{15}H_{12}N_2O,H_2SO_4$, melts at 237°. On treatment of its alkaline solution with sodium nitrite, *isonitrosodiphenylpyrazolone*, $C_3N_2Ph_2O:NOH$ is formed; this melts at 197—200°. *Diphenylpyrazoloneazobenzene*, $C_3HN_2Ph_2O\cdot N_2Ph$, is obtained when diazobenzene chloride is added to a cooled solution of diphenylpyrazolone in acetic acid; it crystallises in matted needles, and melts at 170—171°.

Diphenylpyrazolone, when heated with an excess of benzaldehyde, is converted into *benzylidenediphenylpyrazolone*, $C_3N_2Ph_2O:CHPh$, which crystallises in slender needles, and melts at 147°; when, however, an excess of diphenylpyrazolone is employed, *benzylidene-bis-diphenylpyrazolone*, $C_3HN_2Ph_2O\cdot CHPh\cdot C_3HN_2Ph_2O$, is also obtained; this forms colourless crystals, melting at about 220°. *Bis-diphenylpyrazolone*, $C_{30}H_{22}N_4O_2$, is formed by the oxidation of diphenylpyrazolone with phenylhydrazine at the boiling point; it melts above 330°.

On treatment with methyl alcohol and methyl iodide at 100° in a sealed tube, diphenylpyrazolone yields *diphenylmethylpyrazolone*, $NPh<\begin{matrix}CO—CH\\NMe\cdot CPh\end{matrix}>$. This compound crystallises in white needles, melts at 150°, and is sparingly soluble in hot water, ether, and light petroleum, readily soluble in alcohol and acetic acid. The *hydrochloride*, $C_{16}H_{14}N_2O,HCl$, crystallises in satiny needles, and is decomposed by water; the *ferrocyanide*, $(C_{16}H_{14}N_2O)_2,H_4Fe(CN)_6$, is a white, crystalline precipitate; the *picrate*, $C_{16}H_{14}N_2O,C_6H_2(NO_2)_3OH$, melts at 170°. With bromine, diphenylmethylpyrazolone yields an additive product, which on treatment with water is converted into the substi-

tution derivative $C_{16}H_{13}N_2OBr$; this melts at 110—120°, and is soluble in water. W. P. W.

Weyl's Reaction for Creatinine. By J. Guareschi (*Chem. Centr.*, 1887, 580).—Weyl has shown that a red coloration is produced on the addition of a few drops of sodium nitroprusside and soda to a solution of creatinine; Salkowsky has further shown that the addition of acetic acid causes a bluish-green coloration. According to the author, this reaction is not restricted to creatinine, but is common also to substances allied to it, such as thio- and methyl-hydantoïn, and compounds derived from them. Thus if carbamide or thiocarbamide is melted with an amido-acid, the product gives the above reaction. It is apparently characteristic of compounds containing the glycollyl-group $CH_2{\cdot}CO$, associated with two nitrogen-atoms. V. H. V.

Cryptopine and its Salts. By E. Kauder (*Pharm. J.Trans.* [3], **18**, 250).—To the mother-liquor from which codeïne, narceïne, thebaïne, and papaverine have been separated in the usual way, sodium hydroxide is added in excess, and the resulting precipitate is washed with hot water, and redissolved by hydrochloric acid. The solution on cooling forms a gelatinous mass, which changes in two or three days into soft crystals. These are collected, redissolved in hot water, the hot solution filtered through charcoal, and allowed to cool, when it gelatinises and crystallises. The dried crystals are finally dissolved in hot alcohol, from which on cooling pure white crystals of cryptopine hydrochloride are obtained in soft masses, but without any gelatinous character. From a warm aqueous solution of this salt, ammonia precipitates the alkaloïd in minute crystals. Cryptopine undergoes little or no decomposition when treated with hydrochloric acid, thus differing from other opium alkaloïds. The normal sulphate of cryptopine does not crystallise; the acid sulphate gelatinises as the solution cools, and the jelly shows but slight signs of crystallisation after remaining for weeks. Normal cryptopine meconate is not soluble in cold, but is slightly so in boiling water. The analytical results correspond with the formula $(C_{21}H_{23}NO_5)_2C_7H_4O_7 + 10H_2O$. Probably it is in this form that cryptopine exists in opium, all kinds of which contain it in varying amounts. Its physiological effects have not yet been examined. R. R.

Cinchona Alkaloïds. By W. J. Comstock and W. Koenigs (*Ber.*, **20**, 2510—2527).—The action of bromine on cinchine in chloroform solution (this vol., p. 282) gives rise to two cinchine dibromides in about equal proportions; that already described is now termed α- and its isomeride β-cinchine dibromide. The two compounds can readily be separated by treatment with hot, dilute hydrobromic acid, since the α-dibromide crystallises out in concentrically-grouped needles, whilst the β-dibromide remains in solution. α-Cinchine dibromide crystallises in monoclinic forms; $a:b:c = 0{\cdot}95699 : 1 : 0{\cdot}86861$; $\beta = 65° 52'$; observed faces, $\infty\breve{P}\infty$, ∞P, $\breve{P}\infty$, and $+P$. β-Cinchine dibromide melts at 133—134°, and crystallises in rhombic forms; $a:b:c = 0{\cdot}55524 : 1 : 1{\cdot}2017$; observed

faces, $\breve{P}\infty$, $\bar{P}\infty$, 0P, and $+\frac{2P2}{2}$. The α-dibromide is not converted into the β-compound or *vice versâ* by prolonged heating at 130°, and it is somewhat more soluble in alcohol and ether than its isomeride. Hot dilute nitric acid dissolves the α-dibromide, and the nitrate on cooling separates in colourless crystals; whilst the β-derivative, when similarly treated, is obtained in a form resembling that of recently precipitated silica. Both compounds yield zincochlorides, which crystallise in colourless needles, and melt almost simultaneously at about 250°. The dibromides separated from the nitrates or zinc salts melt at their original temperatures, although both are converted into the same dehydrocinchine on treatment with alcoholic potash.

Cinchonine, on bromination in a mixture of alcohol and chloroform at the ordinary temperature, also yields two dibromides, and these can be separated by the method employed with the α-cinchine-derivatives. The α-dibromide, the isomeride already described (*loc. cit.*), crystallises with 1 mol. H_2O, whilst the β-compound crystallised under similar conditions is always anhydrous. Both derivatives yield sparingly soluble salts, which seem to crystallise differently, and the hydrobromide of the β-compound is more readily soluble in hot, dilute hydrobromic acid.

Chinine dibromide, $C_{20}H_{22}Br_2N_2O$, is obtained by the action of bromine dissolved in chloroform on a chloroform solution of chinine. The *hydrobromide*, $C_{20}H_{22}Br_2N_2O,2HBr + 2H_2O$, is a citron-yellow, crystalline mass, sparingly soluble in cold water, alcohol, and excess of hydrobromic acid. When the base is heated with alcoholic potash for seven to eight hours, it yields *dehydrochinine*, $C_{20}H_{20}N_2O$, which, after repeated recrystallisation of its tartrate, is obtained as a thick oil, slowly solidifying to a mass of long needles. It crystallises with at least 3 mols. H_2O, melts above 40°, and is almost insoluble in water, readily soluble in alcohol, wood-spirit, and ether. The solution in sulphuric acid has an intense greenish-blue fluorescence, and on the addition of chlorine and ammonia becomes green. The *hydrobromide* forms yellow crystals, and is readily soluble in water, less so in alcohol.

Hydrochloroquinine, $C_{20}H_{25}ClN_2O_2$, is formed when quinine hydrochloride is treated with 10 times its weight of hydrochloric acid saturated at −17°, and allowed to remain for a week at the ordinary temperature; the base is precipitated by ammonia and purified by conversion into its nitrate, which is then repeatedly crystallised from very dilute nitric acid. It melts at 186—187°, and is insoluble in water, but crystallises well from ether and alcohol. The *nitrate* forms colourless crystals, is very sparingly soluble in dilute nitric acid, and its aqueous solution fluoresces an intense blue, and gives the green coloration on treatment with chlorine-water and ammonia. *Hydrobromoquinine*, $C_{20}H_{25}BrN_2O_2$, obtained by the action of hydrobromic acid saturated at −17°, on quinine dihydrobromide in the cold, yields a well-crystallised acid hydrochloride and hydrobromide; the latter has the composition $C_{20}H_{25}BrN_2O_2,2HBr$. Neither the hydrochloro- nor the hydrobromo-quinine are soluble in aqueous potash, but on treatment for 50 days at the ordinary temperature with 10 times

its weight of hydrobromic acid saturated at −17°, acid quinine hydrobromide yields a compound, $C_{20}H_{27}Br_3N_2O_2$, which dissolves completely in dilute aqueous potash, and is precipitated from the solution by carbonic anhydride. It is soluble in ether, and its solution in sulphuric acid shows no fluorescence.

Hydrochlorocinchonine, $C_{19}H_{23}ClN_2O$, obtained in a similar manner from cinchonine hydrochloride, melts at 212—213°. The *dihydrochloride* crystallises in well-formed prisms. When the base is heated with alcoholic potash for 10 to 12 hours, it loses chlorine and seems to be converted, like the hydrobromo-derivative, into isocinchonine and a small quantity of cinchonine. Hydrobromocinchonine, $C_{19}H_{23}BrN_2O$, prepared similarly from cinchonine dihydrobromide, is identical with the base obtained by Skraup (*Annalen*, **201**, 324), and when heated with silver oxide, yields as stated by him silver bromide and an organic base of peculiar odour recalling that of acetamide and piperidine; this change, however, does not occur in the cold. The same odour is produced when hydrobromocinchonine is heated with dilute sulphuric acid and lead dioxide or manganese dioxide with the addition of some silver sulphate, and the product afterwards saturated with an alkali; cinchonic acid is also formed during the oxidation with manganese dioxide.

Isocinchonine, $C_{19}H_{22}N_2O$, is formed when hydrobromocinchonine (1 part) is heated in a reflux apparatus with potassium hydroxide (2 parts), and alcohol (30 parts), until the base is free from bromine. At the same time, cinchonine is also obtained, and the two bases are separated by treatment with ether; the small quantity of cinchonine is then removed by converting the residue obtained from the ethereal solution into the zincochloride, and crystallising from aqueous zinc chloride, in which solvent the isocinchonine compound is sparingly soluble in the cold. Isocinchonine melts at 125—127°, and, unlike cinchonine, is extremely soluble in alcohol, ether, benzene, carbon bisulphide, chloroform, and ethyl acetate. With acids, it yields for the most part soluble salts, and when carefully heated in small quantity volatilises without decomposition. The *zincochloride*, $C_{19}H_{22}N_2O,2HCl,ZnCl_2$, crystallises in small, colourless needles and melts at 260—262°.

Hydrobromocinchine, $C_{19}H_{21}BrN_2$, obtained by dissolving cinchine in 10 times its weight of hydrobromic acid saturated in a freezing mixture of ice and salt, and allowing the solution to remain for two days, crystallises from ether in monoclinic forms; $a : b : c = 0{\cdot}85412 : 1 : 0{\cdot}82801$; $\beta = 63° 7'$; and is isomorphous with α-cinchine dibromide (m. p. = 113°). It melts between 105° and 116°, and dissolves readily in alcohol, ether, &c., but only sparingly in light petroleum. The zincochloride crystallises well. Cinchine does not seem to form addition compounds with 2 mols. of a haloïd acid or 2 mols. of bromine. β-Cinchine dibromide, for example, when treated with bromine in chloroform solution, yields a perbromide, which is converted into the unaltered base on the addition of sodium hydrogen sulphite; whilst cinchine, when heated with concentrated hydrobromic acid at 100°, yields a base which could not be crystallised, and which seems to contain somewhat less bromine than hydrobromocinchine.

Hydrobromodehydrocinchonine, $C_{19}H_{21}BrN_2O$, is prepared by allowing a solution of dehydrocinchonine in concentrated hydrobromic acid to remain for eight days. It forms anhydrous crystals, and melts at about 235°. The corresponding dehydrocinchonine dibromide could not be prepared by the action of bromine on dehydrocinchonine in chloroform solution, but under these conditions a crystalline base melting at 228° is obtained, whose composition approximates to that of a monobromodehydrocinchonine, $C_{19}H_{19}BrN_2O$.

Pyridine-derivatives do not seem to form halogenated compounds when treated with hydrobromic acid saturated at −17°; thus pyridine and quinoline are unaltered in the cold or when heated at 140° with the acid; tetrahydroquinoline is unaffected in the cold, and the tertiary base, $C_{11}H_{13}N$, obtained by Fischer and Steche (this vol., pp. 588 and 976), which is probably a partially hydrogenated quinoline-derivative, and methyllepidone are similarly unattacked. From considerations based on the oxidation of cinchonine and quinine with chromic acid, the authors regard it as improbable that the quinoline-group in the molecule is hydrogenated, and since these alkaloids, together with cinchine and dehydrocinchonine, readily combine with a molecule of hydrogen bromide or chloride, it is evident that the addition must occur in the complex $C_{10}H_{16}NO$, which seems to have the same constitution for both alkaloïds. W. P. W.

Preparation of Aconitine. By J. Williams (*Pharm. J. Trans.* [3], **18**, 238—240).—The dried, coarsely ground root of *Aconitum napellus* is exhausted with amyl alcohol, the solution is agitated with very dilute sulphuric acid (1 : 600), the alkaloïd is precipitated from the acid by sodium carbonate, and then dissolved either in alcohol or in ether, and allowed to crystallise. The necessary precautions are detailed in the original. R. R.

Curare. By R. Boehm (*Chem. Centr.*, 1887, 520).—Besides the active principle, curarine, contained in curare, the author has found a second base, *curine*, which has no action on the organism. This is a white, microcrystalline substance, soluble in water, readily soluble in alcohol, chloroform, and in dilute acids. The solutions give a thick, white precipitate with metaphosphoric acid.

The separation of curarine is effected by means of platinic chloride; it is a yellow substance. 0·35 mgrm. is sufficient to kill a rabbit weighing 1 kilo.; 0·003—0·005 mgrm. will kill a frog. N. H. M.

The Alkaloïds of Coca Leaves. By O. Hesse (*Pharm. J. Trans.* [3], **18**, 71).—The author dissents from Stockman's opinion that amorphous cocaïne is a solution of true cocaïne in hygrine. Coca leaves finely divided, and extracted by ether, give on agitation of the ethereal solution with hydrochloric acid, a liquid which although at first non-fluorescent, after a time becomes distinctly fluorescent, thus showing that hygrine is a product of subsequent decomposition. The amorphous bases easily separated from cocaïne, give a platinum salt containing 18·44 per cent. platinum; but these are not homogeneous, for the author has been able to separate by fractional precipitation a

well-defined base, which he has called *cocamine*. This has the same composition as cocaïne, $C_{17}H_{21}NO_4$; it dissolves readily in ether, alcohol, or chloroform, and on evaporation remains in an amorphous condition. Its hydrochloride, $C_{17}H_{21}NO_4,HCl$, is amorphous, neutral, and soluble in water and alcohol; when dried at 120° it loses weight, and eventually becomes insoluble in cold water. R. R.

Separation of Hygrine from Cocaïne. By W. C. Howard (*Pharm. J. Trans.* [3], **18**, 71).—In a liquor containing cocaïne, hygrine, &c., neutralised by hydrochloric acid, platinum chloride produces a doubtfully semi-crystalline precipitate, part of which was insoluble in water at 80°. The base of the soluble part, the author identified as cocaïne. The insoluble platinum salt was found by two experiments to contain platinum, 18·48 per cent. and 18·6 per cent., and when decomposed in the usual way, it yielded a base that gave no crystallisable chloride, did not smell of trimethylamine, had a bitter taste, and was not decomposed by hot water; in which characters it differs from hygrine as described by Lossen (*Annalen*, **121**, 374). Therefore, either Lossen's base was impure, or the author's is a different one, and amorphous cocaïne may have no existence, but may be merely a solution of cocaïne in the base above described.

R. R.

Higher Homologues of Cocaïne. By F. G. Novy (*Pharm. J. Trans.* [3], **18**, 233—234).—These substances were prepared by heating benzoylecgonine with the homologues of methyl iodide.

Ethylbenzoylecgonine, $C_{16}H_{18}EtNO_4$, forms white, silky crystals or large monoclinic prisms, melts at 107—108°, and resolidifies at 90°. The hydrochloride crystallises in colourless needles or prisms; the platinochloride, $(C_{18}H_{23}NO_4)_2,H_2PtCl_6$, forms yellow, rhombic plates; the aurochloride is obtained as a voluminous, yellowish-white precipitate. Bromethylbenzoylecgonine, prepared from benzoylecgonine and ethylene bromide, $C_2H_4Br\cdot C_{16}H_{18}NO_4$, could only be obtained as a colourless syrup.

Propylbenzoylecgonine, $C_{16}H_{18}PrNO_4$, crystallises in silky needles or colourless prisms, melts at 78—79·5°, and resolidifies at 65°; it has a very bitter taste and is a powerful anæsthetic.

Isobutylbenzoylecgonine, $C_4H_9\cdot C_{16}H_{18}NO_4$, crystallises in short, colourless prisms, melts at 61—62°, has an intensely bitter taste and powerfully anæsthetic properties. The hydrochloride forms a hard, vitreous, yellow mass. A. J. G.

Absorption of Light by Oxyhæmoglobin. By F. Krüger (*Zeit. Biol.*, **24**, 47—66).—The results of the present investigation corroborate Kupffer's statement that the absorption coefficient of oxyhæmoglobin increases each time the oxyhæmoglobin is recrystallised.

In determining the absolute amount of hæmoglobin in blood by means of the spectrophotometer, it is best only to recrystallise once, as each recrystallisation increases the error of observation.

The use of dilute ammonia in the preparation of hæmoglobin

crystals as recommended by Schmidt increases their solubility in water. J. P. L.

Action of Reducing Agents on Hæmatin and Occurrence of the Products of Reduction in Pathological Urine. By C. Le Nobel (*Chem. Centr.*, 1887, 538).—When hæmatin is reduced in acid or alkaline solution, iron is eliminated and *hæmatoporphyrin* is formed. Afterwards *hæmatoporphyroïdin* (differing from hæmatoporphyrin in solubility but nearly identical in its spectroscopic properties) is formed. The hæmatoporphyroïdin is then transformed into Mac-Munn's urohæmatin, to which the author gives the name *isohæmatoporphyrin* and lastly *urobilinoïdin* is formed. This resembles urobilin in some of its properties; it can readily be converted into isohæmatoporphyrin and hexahydrohæmatoporphyrin. Maly's hydrobilirubin is not identical with Jaffe's urobilin. There is no connection between the colouring matter of blood and Jaffe's urobilin. In some pathological conditions, in which it may be assumed the colouring matter of blood has decomposed, the above products of reduction occur in urine. N. H. M.

Hemialbumose. By Axenfeld (*Arch. Pharm.* [3], **25**, 696—697).—Pyrogallol is a better precipitant for this albuminoïd than either ammonium sulphate, or nitric or picric acids, as more dilute solutions can be employed. Its sensibility is 10 times that of nitric acid. The author has detected hemialbumose in meal, bread, leguminous seeds, milk, and cheese. The usual method of detection consists in the precipitation of hemialbumose at the ordinary temperature by nitric acid, and solution of this precipitate on warming, but the pyrogallol test succeeds where this test fails. In milk after precipitating the caseïn by acetic acid, and the albumin and paraglobulin by magnesium sulphate, 0·13 per cent. of hemialbumose was found in cow's milk and 0·29 per cent. in human milk. All animal tissues excepting nerve and muscle substance contain hemialbumose. J. T.

Physiological Chemistry.

Glycogen. By A. Cramer (*Zeit. Biol.*, **24**, 67—104).—The potash process for estimating glycogen recommended by Külz, has enabled the author to make an exhaustive study of the occurrence and relative distribution of glycogen in various tissues and organs. The following are some of the chief conclusions arrived at:—

From the result of many determinations, the process leaves little to be desired from the point of accuracy.

The glycogen in the muscular structure of both halves of the body is found, as would be supposed from theoretical considerations, to be equal. In the liver, the glycogen is equally distributed throughout: for the estimation of the glycogen therefore it is only necessary to

use a small portion. In the muscles of the heart, glycogen is unequally distributed, therefore the whole organ must be taken for the determination.

Different groups of muscles vary in the amount of glycogen they contain, but symmetrical or corresponding muscles contain the same amount.

Absolutely pure glycogen can be obtained from the skin of the human fœtus or the cartilage of the fœtus of an animal.

In the estimation of the total amount of glycogen in the body, it is only necessary, as Böhn and Hoffmann have already pointed out, to take into consideration the glycogen in the muscular mass and liver, for the amount existing in other organs is not of sufficient importance.

Lastly, the optical method proposed by Kulz is not so accurate as the method of weighing. J. P. L.

Chemical Studies on the Torpedo. By T. Wayl (*Zeit. physiol. Chem.*, **11**, 525—528).—From the electrical organ of the torpedo, a substance, *torpedo-mucin*, can be separated in the following way:—The organ is first extracted with cold, then with hot alcohol and ether; the residue is then cut into small pieces and extracted with dilute sodium hydroxide (0·1 per cent.). A solution is obtained of a faint-yellow colour, which is filtered and diluted with distilled water. On adding very dilute acetic acid to this, a white, flocculent precipitate is obtained; this is washed by decantation, redissolved in sodium and hydroxide, reprecipitated by acetic acid. After this process has been repeated five times, the precipitate is washed with alcohol, and dried, first in a vacuum over sulphuric acid, and then at 110°. An elementary analysis gave the following results:—

I. Containing ash: II. Free from ash.

	C.	H.	N.	O.	S.	Ash.
I.	51.60	7·09	13·00	25·46	1·02	1·83
II.	52·50	7·2	13·20	26·07	1·03	—

The ash contained lime, magnesia, and phosphoric acid. This substance has the following properties: it is completely soluble in alkalis and is precipitable from such solutions by acetic acid; neutralisation with hydrochloric acid produces a precipitate soluble in excess of acid or alkali; it is precipitated from its solution in dilute hydrochloric acid by saturation with sodium chloride; when heated with sulphuric or hydrochloric acid, it yields no substance which reduces copper sulphate; the solution in dilute sodium hydroxide is coloured red by a drop of copper sulphate solution; but on boiling no reduction occurs. A mucin with similar properties is also obtained from the fresh organ after its extraction with alcohol and ether. Gelatin was obtained also from the organ, best from the residue left after extraction with sodium hydroxide. The fresh organ yields a very small quantity of a globulin which can be extracted by a solution of sodium chloride or ammonium chloride. This is coagulated by heat at 55—60° C.

Abundant proteïd can however be obtained after the exposure of the organ to the air for some time; an acid reaction is also developed simultaneously. Probably the mucin yields a proteïd as a decomposition product. W. D. H.

Nitrogenous Contents of the Digestive Juices. By Ellenberger and Hofmeister (*Zeit. physiol. Chem.*, **11**, 497—500).—This investigation was carried out in the same way as Goldschmidt's (this vol., p. 743), except that the food given was in all cases free from nitrogen.

Three animals—one pig and two horses—were fed for some days on a diet poor in nitrogen, then for 24 to 36 hours on water only, and finally for three days in the case of the horses, and 36 hours in the case of the pig, on a diet consisting of starch and cellulose, free from nitrogen.

The animals were killed, and the stomach and small intestines were found to be free from food containing nitrogen; the colon and rectum, and in one horse the cæcum, also contained remains of the first diet. The following table gives the results of the analysis of the digestive juices in various parts of the alimentary canal:—

	Amount of Proteïd in			
	Stomach.	Small intestine.	Cæcum.	Colon.
Pig	1·4 gr.	16·32 gr.	1·551 gr.	4·6 gr.
Horse 1 ..	13·3 „	10·08 „	17·3 „	49·79 „
Horse 2 ..	6·14 „	43·5 „	17·97 „	—

	Percentage of Nitrogen in			
	Stomach.	Small intestine.	Cæcum.	Colon.
Pig	0·3 gr.	4·80 gr.	0·47 gr.	0·50 gr.
Horse 1 ..	1·4 „	0·28 „	0·17 „	0·25 „
Horse 2 ..	1·17 „	1·00 „	0·19 „	—

The large quantity of nitrogen in the small intestine of horse 2 was due to an excessive amount of mucous and epithelial *débris*; and the high percentage of nitrogen in the stomach of the horse compared with that of the pig, was due to the fact that the horses were killed a long time after a meal, so that the saliva had been absorbed, and only the gastric juice, which is rich in nitrogen, was present.

W. D. H.

Relation of Proteïds to Digestive Ferments. By A. Stutzer (*Zeit. physiol. Chem.*, **11**, 529—536).—Previous researches having shown that the results of the natural and artificial digestion of proteïds agree closely (this vol., p. 167), the present further investigations were undertaken as a preliminary to extending the process to the investigation of the digestion of carbohydrates and of mixtures of proteïd and carbohydrate material. These investigations were necessary, as the percentage of acid used (1 per cent. HCl) in the previous experiments is too high for experiments in which the digestion of carbohydrates is expected to take place. Meat freed from fat,

two kinds of hay, and cake made from the seeds of *Arachis hypogæa* were the forms of food employed. A given weight (1 or 2 grams) was subjected to the action of different amounts of pepsin solution containing 0·2 per cent. HCl for 12 hours at the temperature of 37—40°.

It was found by estimating the undigested nitrogen that the optimum of pepsin digestion under these circumstances was obtained when the nitrogen in the food was—

	5 per cent.,	by	100 c.c. of	pepsin	solution,
5—10	„	„	200	„	„
over 10	„	„	400	„	„

to every gram of the food.

On comparing the amount of nitrogen in the undigested residue with that left when 1 per cent. HCl was employed, it was found to be somewhat less in the latter case, as is shown by the following table :—

Nitrogen left in the undigested residue—

	When 1 p. c. HCl was used.	When 0·2 p. c. HCl was used.
Flesh	0·375 p. c.	0·375 p. c.
Hay 1	0·339 „	0·390 „
Hay 2	0·282 „	0·340 „

The next point investigated was how much nitrogen remains undigested on treating the fodder successively with an acid pepsin solution and an alkaline pancreatic liquid, first when the pepsin solution has an acidity of 0·2 per cent. HCl, and secondly when it has an acidity of 1 per cent. HCl. It was found that the difference was so small as to be inappreciable.

The last question related to the comparative activity of the pancreatic ferment when the solution is neutral and feebly alkaline (containing 0·25 per cent. of sodium carbonate), and in all cases it was found that the alkaline fluid was the more active.

W. D. H.

Comparative Absorption of Fish and Meat in the Alimentary Canal. By W. O. Atwater (*Zeit. Biol.*, **24**, 16—28).—During an inquiry into the chemical composition of fish-flesh undertaken on behalf of the United States Fishery Commission, the author investigated the comparative nutritive value of fish and meat as nitrogenous food, by a series of feeding experiments in which a careful determination of the nitrogen intake and output was made.

Weight for weight in dry matter, fish is equivalent to lean or fat-free meat as a source of nitrogenous food.

In the opinion of the author the importance of fish as a food for the mass cannot be too strongly emphasised. J. P. L.

Digestion of Fibrin by Trypsin. A. Herrmann (*Zeit. physiol. Chem.*, **11**, 508—524).—Hasebroek (this vol., p. 609) has shown that the first products of the tryptic, like those of the peptic digestion of fresh fibrin, are two proteïds which coagulate at 52—54° and 72—75°

respectively. Otto (Abstr., 1884, 1056) has also shown that the latter is identical with paraglobulin. The present research is a further investigation of the same subject, as it seems remarkable that whilst fibrin is undoubtedly formed from fibrinogen, it should yield paraglobulin on digestion. Fibrin was well washed with water, and subjected to artificial pancreatic digestion at the body temperature for 24 hours, or in some cases for a longer time at the atmospheric temperature. After this time, a small portion only was left undissolved. Putrefaction was prevented in these experiments by the addition of thymol, or of ether sufficient to give the whole mixture a strong ethereal odour. The fluid product of digestion was saturated with magnesium sulphate; this produced an abundant precipitate, which was collected and dissolved by adding water; the solution so formed was a clear, slightly yellow liquid, and from it, by fractional heat coagulation, two proteïds, one coagulating at 54—55°, and another at 75°, were obtained. There was also a slight opalescence at 61°, probably produced by a small amount of heteroalbumose; the presence of albumoses was also detected by the biuret reaction after the separation of the proteïds coagulable by heat. Both proteïds were also shown to belong to this class of globulins by the fact that they were precipitated by dialysing the salts out from their solutions. By extracting fibrin with a 5 per cent. salt solution, a proteïd coagulating at 75° and having the other properties of paraglobulin is obtained. The other globulin, that which coagulates at 55°, is, however, undoubtedly a product of ferment action; it is always the more abundant of the two, and the more thoroughly that fibrin is washed free from paraglobulin by salt solution previous to digestion, the less is the amount of paraglobulin in the product of digestion. The question whether this globulin coagulating at 55° is identical with either of the two proteïds, fibrinogen or myosin, which coagulate at the same temperature, was not fully investigated. Its specific rotation was estimated as $[\alpha]_D = 36{\cdot}39°$; whilst that of fibrinogen prepared by Hammarsten's method was $[\alpha]_D = 43°$. Too much weight must not be attached to these numbers, as the opalescent character of fibrinogen solutions renders polarimetric observations difficult.

Attempts to cause coagulation of the proteïd by the action of fibrin ferment led to negative results.

Boiled fibrin does not yield this product on digestion; neither does serum-albumin, caseïn, nor phytovitellin. W. D. H.

Fermentation of Cellulose. By H. Tappeiner (*Zeit. Biol.*, **24**, 105—119).—From exact quantitative experiments on the digestion of cellulose by the organised ferment contained in paunch contents, it is found that a small quantity of the carbon of the cellulose decomposed is not accounted for by the products hitherto mentioned. At present, the author has not detected the product or products formed by this residual carbon.

Asparagine when added to Naegali's cultivating fluid, which was used in some of the fermentation experiments, acts somewhat curiously. When present in small quantity (0·6 per cent.), it does not undergo any decomposition itself or influence the decomposition of the cellu-

lose. When present in somewhat larger proportion (1·8 per cent.), part of the asparagine undergoes decomposition with the cellulose. If the percentage of asparagine is as much as 3·5 per cent., it readily undergoes decomposition with formation of carbonic anhydride, nitrogen, volatile fatty acids, and succinic acid, but, in this instance, the cellulose undergoes no decomposition.

A similar peculiarity is observed in the case of ammonium acetate. 1 per cent. of ammonium acetate in Naegali's solution undergoes no decomposition when the solution is infected with a small quantity of paunch contents in the absence of cellulose, but, in the presence of cellulose, rapid decomposition of the acetate takes place without any action whatever on the cellulose. J. P. L.

Aromatic Products of Putrefaction in Human Sweat. By A Kast (*Zeit. physiol. Chem.*, **11**, 501—507).—The analysis of the sweat is important because of the correlative functions of the skin and kidneys. The occurrence of indigo compounds in cases of *chromidrosis* has already been noted (Bizio, H. B. Hofmann), and Buisine (*Compt. rend.*, **103**, 66), has shown that phenolsulphonic acid exists in the sweat of the sheep. In the present research, by the use of hot air-baths, large quantities of sweat were collected; about 18 to 20 litres in all. Excess of absolute alcohol was added, and sodium carbonate until it was faintly alkaline; it was then evaporated to a small volume on the water-bath. The relation of sulphuric acid (A) combined as sulphate to that combined as ethereal hydrogen sulphates (B) was then estimated with the following results:—

In 200 c.c. of the concentrated sweat (= 10—12 litres of sweat), A = 0·2422, B = 0·022; $\frac{B}{A} = \frac{1}{12·009}$. In the urine of the same individuals collected at the same time, in 200 c.c. of unconcentrated urine A = 0·718, B = 0·448; $\frac{B}{A} = \frac{1}{16·02}$. By administering 10 grains of salol in three days to the same individuals, the quantity of the ethereal hydrogen sulphates in the urine was much increased; $\frac{B}{A} = \frac{1·339}{1}$, whilst in the sweat, $\frac{A}{B} = \frac{1}{9·504}$: in other words the sweat, unlike the urine, remains fairly constant in composition. With regard to the other salts, the following relation was found to exist:—

	Chlorides.		Phosphates.		Sulphates.
Sweat	1	:	0·0015	:	0·009
Urine	1	:	0·132	:	0·397

Favre (*Compt. rend.*, **35**, 721) gives the following relations:—

	Chlorides.		Phosphates.		Sulphates.
Sweat	1	:	traces	:	0·043
Urine	1	:	0·0959	:	0·38

By the distillation of sweat, phenol was easily obtained, and

recognised by Millon's reagent. Another portion of sweat was acidified with hydrochloric acid, shaken with ether, the ethereal extract evaporated to dryness, and the residue taken up with water; this solution showed the presence of aromatic oxy-acids by the red colour produced by Millon's reagent. Indoxylsulphuric acid was sought for by Jaffe's test, with negative results; the same test gave, however, a red colour, showing the presence of scatoxyl. It is suggested that the blue colour of the sweat in chromidrosis is due to bacteria. W. D. H.

Relation of Tyrosine to Hippuric Acid. By K. Baas (*Zeit. physiol. Chem.*, **11**, 485—491).—Many aromatic compounds which occur in the urine have been shown to be decomposition products of tyrosine formed in the alimentary canal. The question as to whether hippuric acid is derived from tyrosine also, has been investigated by Salkowski, Schotten, and Baumann, but the results obtained have been somewhat contradictory. The present research was carried out in human beings, and consisted in comparing the normal urine with that secreted during the administration of tyrosine. The hippuric acid was estimated by Schmiedeberg and Bunge's method; and the amount of sulphates and ethereal hydrogen sulphates by Baumann's method. The experiments show that giving tyrosine did not alter the amount of hippuric acid in the urine, and therefore that the normal formation of that acid does not result from the tyrosine in the intestine. The conclusion is also drawn that tyrosine does not always undergo putrefactive decomposition in the alimentary canal, but that in spite of the presence of bacteria, it may be wholly absorbed as such. W. D. H.

Urinary Pigments. By L. v. Udránszky (*Zeit. physiol. Chem.*, **11**, 537—560).—On looking over the literature of the subject of urinary pigments, which extends from the beginning of the present century, it is found that the following conclusions can be drawn from the work at present done on the subject:—(1.) By the action of oxidising agents, indigo-blue and other indigo compounds, for example, indirubin, can be obtained from normal urine. (2.) In most cases urobilin, which is identical with hydrobilirubin, is also present. (3.) In addition to the foregoing, pigments are obtained by boiling the urine with mineral acids, and are probably derived from the splitting up of certain chromogens in the urine by these strong reagents: to one of these, the name uromelamin is given. It is to the investigation of this third class of pigments that the present research is mainly directed. A litre of normal urine was heated for a quarter of an hour with 5 per cent. hydrochloric acid, and extracted with amyl alcohol; on evaporating the alcoholic extract, a brownish-black, amorphous residue was obtained weighing 0·68 gram. This is the ordinarily received method of obtaining this pigment. The experiment was repeated, using distilled water instead of urine, and a residue weighing 0·51 gram was obtained, having the same characters, including spectroscopic appearances. The prolonged action of hydrochloric acid in the cold has the same action on amyl alcohol. What this resinous substance is was not further investigated;

it was found, however, that the alcohol after distillation still possessed the same action on polarised light as previous to the separation of the pigment from it. This admixture of the resinous substance from the reagents used with the urinary pigment could not be prevented by attempting to wash the acid away from the alcohol by the use of water; it was not found possible to remove the acid in this way. By neutralising the mixture with chalk, however, the author considers he has been able to obviate this source of error. On account, however, of the unsatisfactory nature of amyl alcohol as a reagent, a method was sought for in which it was not necessary to employ it. The method ultimately adopted was as follows:—Normal urine was evaporated to about one-sixth of its original bulk at 60°; 10 per cent. hydrochloric acid was then added, and after 48 hours the crystals of uric acid thus formed were filtered off. The filtrate was boiled for 18 hours, at the end of which time the remains of the uric acid with an abundance of pigment were precipitated; the filtrate had an orange-red colour; to this, chalk and sodium phosphate were added; the bulky precipitate which was formed carried down with it the remains of pigment. The precipitate obtained from the urine by boiling was washed with cold water, hot water, alcohol, and ether, dissolved in dilute sodium hydroxide solution, and precipitated by sulphuric acid. This was repeated three times, and the final product was a bright, brownish-black substance, occurring in plates, but easily powdered. It was insoluble in cold water, dilute alcohol, ether, and chloroform, sparingly soluble in warm water, absolute alcohol, light petroleum, and concentrated sulphuric and hydrochloric acids. It was easily soluble in amyl alcohol, concentrated ammonia, but especially in solutions of potassium or sodium hydroxide. It can be heated to 115° without decomposition; with soda-lime it yields ammonia; on dry distillation, it gives a smell of formic acid, and after complete combustion leaves a minimal amount of ash which contains no iron. The average quantity in which it occurs in urine is 0·03 per cent. By the action of potash, it yields ammonia, formic acid, acetic acid, butyric acid, palmitic acid (?), catechol, protocatechuic acid, and the residue is free from nitrogen, and has the following percentage composition:—Carbon, 62·26; hydrogen, 3·9; and oxygen, 33·84. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrifying Microbes. By M. Miles (*Bied. Centr.*, 1887, 514—515). —Miles confirms Warington's observation as to the length of time which elapses between the infection of the liquid and the commencement of the nitrifying process, and he finds that this period of quiescence may be cut short by introducing a minute quantity of another and earlier culture. When calcium carbonate was absent, the microbes increased rapidly, but nitrification seldom occurred, and microbes which had been cultivated for some generations in liquid not containing calcium

carbonate, caused nitrification in dilute urine to which calcium carbonate had been added. It appears that those microbes which increase rapidly without nitrification are of peculiar aërobic forms, but if they cause rapid nitrification, then they belong to the anaërobic class. Solutions were tested for nitrous acid, but it was seldom found; when found it was in those solutions which gave no reaction for nitric acid, and in which micrococci appeared together with the true nitrifying microbe. E. W. P.

Culture of Anaërobic Bacteria. Morphology of Butyric Fermentation. By M. Gruber (*Chem. Centr.*, 1887, 535).—Gelatin, contained in a glass tube about 2 cm. wide, fused together at one end and drawn out to a neck 5 to 6 cm. long, and 3 to 4 cm. wide, is inoculated, the tube placed in water at 30—35°, exhausted and sealed. The fused gelatin is spread over the surface of the tube by rotation. In using this method, the author found that the three bacteria known by the joint name of *Clostridium butyricum* (*Bac. amylobacter*), are capable of producing butyric acid and butyl alcohol from carbohydrates. N. H. M.

Distribution of the Nitric Ferment and its Function in the Disintegration of Rocks. By A. Müntz (*Ann. Chim. Phys.* [6], **11**, 136—144).—The bare surfaces of calcareous, felspathic, micaceous, schistose, and other rocks at the summits of mountains in the Pyrenees, Alps, and Vosges, yielded large numbers of the nitric ferment, which penetrates to a considerable depth in the cracks in the rocks, and is especially abundant on surfaces which show the greatest disintegration. This organism is not killed by the lowest temperatures of the Alps.

The rocks concerned, especially those above the limits of vegetation, contain small quantities of carbon, which make the rock blacken when heated. This carbon is derived from air and rain. The author has previously proved that alcohol vapour exists in small quantities in the atmosphere. Direct experiments show that the nitrifying organisms will exist and produce nitrates with no other sustenance than the mineral constituents of the rock on which they are placed and small quantities of alcohol vapour and ammonia suspended in a moist atmosphere. Some carbon is also found to have been deposited in or upon the rock on which the organisms are living. There is every reason to believe that these nitrifying organisms play an important part in the superficial disintegration of rocks even at the highest levels. C. H. B.

Methane Fermentation of Acetic Acid. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **11**, 561—568).—Calcium acetate was dissolved in water, and river mud added to the solution in a flask. The mixture was allowed to stand at the atmospheric temperature for seven months, during which time the gas which was evolved was collected over mercury and occasionally analysed. For the first few weeks, some atmospheric nitrogen was present in the mixed gases, but after this time carbonic anhydride and methane were alone present, in the

proportion 1 : 2 approximately. The residue in the flask consisted almost entirely of calcium carbonate. The decomposition which had occurred may be represented thus: $(C_2H_3O_2)_2Ca + H_2O = CO_3Ca + CO_2 + 2CH_4$. In addition to the calcium carbonate, there was also in the flask a small amount of sodium carbonate: this was derived from a slight impurity in the original salt used, together with some derived from the glass wall of the flask. There was also organic matter from the mud, and a large number of bacteria. The change is believed to be due to the agency of the bacteria, although to which special variety has not yet been ascertained. By an experiment similarly carried out with calcium lactate, carbonic anhydride and methane in the proportion of 1 : 2 were evolved, the residue being composed of calcium acetate. It is possible, therefore, that methane in the alimentary canal is not always derived from cellulose.

W. D. H.

Formation of Starch in the Chlorophyll Granules. By G. Belluci (*Chem. Centr.*, 1887, 572).—In order to determine whether the production of starch under the influence of sunlight, and the subsequent reconversion during night time, is to be regarded as a physiological or as a chemical change, the effect of the presence of various substances was tried. Chloroform, and to a slighter extent, ether vapour, destroy chlorophyll, and also prevent the transformation of starch formed during sunlight; carbonic anhydride also diminishes the function of the chlorophyll, but does not destroy it, if the action is not allowed to continue unintermittently for 24 hours. The saccharification of starch proceeds in the dark, even in cut-off leaves, but more rapidly with free access of air. From these experiments, the author concludes that the phenomenon is a physiological and not a chemical change.

V. H. V.

Crystalline Deposits in Dahlia Tubers. By H. Leitgeb (*Ann. Agronom.*, **13**, 378—379).—In order to exhibit the sphero-crystals of inulin, the common plan is to soak sections of dahlia tubers in alcohol. The author having allowed a tuber to soak for several years in this liquid, finds the spheres of inulin with radial striæ grouped in the peripheral region of the tuber. But besides these he has noticed spheres composed of an amorphous nucleus surrounded by an envelope formed of radiating needles. These crystals abounded in the pith and inner portions of the parenchyma. They leave after combustion a mineral residue of the same shape as the crystals, consisting of calcium phosphate. The amorphous nucleus consists of an organic substance which is neither inulin nor fatty matter.

J. M. H. M.

Absorption of Ammonia by Clay. By W. Wipprecht (*Bied. Centr.*, 1887, 517—518).—The experiments were made on a clay from Texas. All ammonia was removed from the clay previous to the experiments by heating at 400°. The following conclusions are drawn. Moist clay contains more ammonia than drier clay. If the moisture remains constant, the more ammonia is absorbed the longer the clay remains exposed to the air. Dried clay when moistened and exposed for one day to the air, absorbs a considerable quantity

of ammonia. When moist clay is exposed to air, the loss of water is accompanied with a proportionately greater loss of ammonia; on the other hand, when clay is absorbing water from the air, it at first gains more ammonia than it would lose during the evaporation of the same amount of water. A. J. G.

Analysis of Onions. By C. A. Goessmann (*Pharm. J. Trans.* [3], **18**, 77—78).—1000 parts of air-dried onions, without the leaves, consisted of 892 parts of water, and 108 of dry matter, containing 2·12 parts of nitrogen, 0·48 part of sulphur, and yielding 4·36 parts of ash. The percentage composition of the ash was—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	SiO_2.	P_2O_5.
38·51	1·90	8·20	3·65	0·58	3·33	15·80

The sulphuric acid in the ash was not determined, because the 0·48 part of sulphur in 1000 parts of the onion includes the total amount of sulphur present in any form. Whilst sulphur is an essential constituent of all plants, it is only in a comparatively few families that it exists in volatile combinations capable of imparting strong and offensive odours. As many plants of this kind when eaten by cows impart their odour to the milk, their absence is one condition of good dairy farm pastures. R. R.

Manurial Experiments with Various Phosphates. By Kremp (*Bied. Centr.*, 1887, 525—527).—The crop was oats, and various phosphates:—super, precipitated and basic cinder, were used in combination with Chili saltpetre. Very little or no gain was obtained by the addition of the phosphates. Analyses of the soil are not given. E. W. P.

Manuring with Various Phosphates. By W. Roberts (*Bied. Centr.*, 1887, 528—530).—Superphosphate was compared with precipitated and Ardennes phosphates as to its action on the growth of wheat. The Ardennes produced an intermediate crop, whilst that from the use of the precipitated phosphate was only an eighth of the net gain by the use of superphosphate. Further experiments on potatoes, roots, and buckwheat showed a similar result, the reduced phosphate lagging far behind. E. W. P.

Analytical Chemistry.

Improved Form of Elliott's Gas Apparatus. By J. B. Mackintosh (*Amer. Chem. J.*, **9**, 294—296; compare Abstr., 1884, 215).—The measuring tube is provided at the top with a three-way stopcock, and is thus permanently connected on the one side with the absorption burette, on the other with the explosion burette, the small funnel for the top of which is no longer required.

A convenient method of preparing oxygen for gas analysis is by the

action of hydrogen peroxide on an acidified permanganate solution in the absorption burette. H. B.

New Mode of Testing for Nitrates. By E. Bréal (*Ann. Agronom.*, **13**, 322—327).—The author utilises the tendency of dissolved nitrates to accumulate in capillary spaces, or where evaporation is most active. One end of a strip of white filter-paper is immersed in the solution to be tested, the other end being freely exposed to the air. After the lapse of 12 to 15 hours, if the solution contained only traces of nitrates, these will be found entirely concentrated within a millimetre of the free end of the strip of paper. This is cut off, dried on a white surface, and moistened with a drop of phenolsulphonic acid, made by adding one part of crystallised phenol to one part of recently boiled pure sulphuric acid and diluting with two parts pure distilled water. A more or less intense red coloration indicates nitrates; when a drop or two of ammonia is added the colour changes to an intense blue or green. The filter-paper employed must be purified by repeated washing with pure distilled water. The delicacy of the test is considerable. One drop of a solution containing 1 mgrm. of potassium nitrate in 1 c.c. of water gives with phenolsulphonic acid an intense red coloration; this drop will contain about 0·025 mgrm. of nitric acid. If one drop of this solution is added to 100 c.c. of water, and the strip of filter-paper immersed in it, nitric acid may be distinctly recognised after 12 hours in the millimetre of paper nearest the free end. This method, therefore, affords the means of detecting a quarter of a mgrm. of nitric acid in a litre of water, or 1 in 4,000,000. If the strip of paper be partly immersed in moist soil, any nitrates in the soil can be very easily detected, and the method promises to become of much use in experiments on the relation of nitrates to plant growth. J. M. H. M.

Detection of Potassium by means of Sodium Bismuth Thiosulphate. By C. Pauly (*Chem. Centr.*, 1887, 553).—The author has reinvestigated this reaction, first proposed by Carnot, and finds that it is really characteristic for potassium, and can be applied without previous separation from most other metals. It consists in adding an alcoholic solution of sodium bismuth thiosulphate, when a yellow, crystalline precipitate of potassium bismuth thiosulphate, $K_3Bi(S_2O_3)_3$, is obtained. A. J. G.

Determination of Alkaline Chlorides in Potashes. By H. Focke (*Chem. Centr.*, 1887, 699).—In order to determine the proportion of sodium and potassium chlorides in potashes, the dissolved sample is neutralised with dilute sulphuric acid, a few drops of normal soda added, and the whole evaporated. The residue is taken up with 85 per cent. alcohol, the water required for the dilution of the alcohol being poured on the mass, and then the absolute alcohol added gradually. After a time, the liquid is filtered, and the insoluble portion washed with alcohol; the mixed solutions are then evaporated, the residue dissolved in water, and the proportion of alkali-metal, and chlorine determined in aliquot proportions respectively. V. H. V.

Testing Copper Sulphate. By Baudoin (*Ann. Agronom.*, **13**, 319—321).—Copper sulphate being now largely employed for application to vines, it becomes of importance to test commercial samples, especially for the sulphates of iron, zinc, and magnesium. Iron is of course easily detected by boiling the solution with nitric acid and adding excess of ammonia. Zinc is best detected by Chancel's process; sodium hyposulphite is added to the solution of the copper sulphate until the latter is decolorised, sodium carbonate is then added, which precipitates both zinc and magnesium if present. They can be separated in the usual way. The author is engaged in ascertaining whether the density of commercial samples of copper sulphate may be utilised as indications of purity. J. M. H. M.

Analysis of Clay. By C. Meineke (*Chem. Centr.*, 1887, 553).—The clay is fused with hydrogen sodium carbonate, the product treated with hydrochloric acid, evaporated to dryness, and heated for some time at 150—300°. It is then dissolved in cold water, decanted five times, and the silica washed on a filter. After ignition, the silica is again evaporated with hydrochloric acid and washed. The weighed silica is treated with hydrofluoric acid, the alumina and ferric oxide determined, and the weight deducted.

The filtrate is evaporated in a platinum dish, when a residue is obtained insoluble in hydrochloric acid, and consisting of silica and alumina.

Sand is determined in the residue obtained by decomposing the clay with sulphuric acid. The residue is dried at not too high a temperature, and exposed to air until no further increase in weight takes place during weighing. The greater part of the residue is weighed, and divided into two nearly equal portions, the one (*a*) is ignited, the other (*b*) is extracted with boiling alkali. From the weight of (*a*) the weight of (*b*) when anhydrous is calculated. The filtrate (*c*) with the rest of the residue is now ignited, and thus the whole weight of anhydrous residue and the proportion $a : b : c\ (a + b + c)$ in the dry and anhydrous state is obtained. N. H. M.

Determination of Manganese by means of Mercuric Oxide and Bromine. By C. Meineke (*Chem. Centr.*, 1887, 554).—Volhard's method is modified as follows:—The solution in nitric or sulphuric acid containing iron as well as manganese to be determined, is precipitated with zinc oxide and made up to a definite bulk. An aliquot part of the solution is treated in the following manner:—Mercuric oxide rubbed with water and bromine-water are alternately added until the former is in considerable excess, when a sudden separation of manganese occurs. The manganese peroxide adhering to the sides of the vessel is dissolved in hydrochloric acid and treated separately. The precipitate is mixed with the oxides of iron and zinc, but is free from manganous oxide. The pure manganic oxide is determined volumetrically by reducing with oxalic acid mixed with hydrochloric acid (eq. mols.), and determining the excess of oxalic acid with permanganate. N. H. M.

Estimation of Metallic Iron in Slags. By G. Neumann (*Zeit. anal. Chem.*, **26**, 530—534).—The usual process, which consists in digesting the slag with copper sulphate and ascertaining the quantity of copper deposited, is accurate in the absence of other reducing agents but is tedious. The measurement of the hydrogen evolved by the substance when treated with a dilute acid gives equally accurate results, and is much more rapid. The ferric oxide present seems to remain inert. A special apparatus for the purpose (for which the unfortunate name "hydrometer" is proposed) consists of a graduated tube with a stopcock-funnel at the top, and a wide-bore (5 mm.) stopcock at the bottom. A narrow tube inserted at the side in an upward direction just above the lower stopcock communicates with a pressure tube like that of the nitrometer. The flask containing the substance is connected directly with the lower end of the graduated tube which is widened to the size of the neck, and is filled to the lower stopcock with water. The graduated tube is then filled through the pressure tube with acid which, on opening the stopcock, finds its way down to the slag. The gas rises through the stopcock into the burette. Any carbonic anhydride or hydrogen sulphide can be absorbed by running in potash through the stopcock-funnel until the contents of the burette are alkaline. M. J. S.

Rapid Methods for the Estimation of Silicon, Sulphur, and Manganese in Iron and Steel. By J. J. Morgan (*Chem. News*, **56**, 82—83).—Silicon is estimated by the so-called "roasting" method, heating in a muffle at a bright-red heat for 20 minutes, treating with hydrochloric acid, and igniting the insoluble silica, &c.

For the estimation of sulphur, the sample is treated with sulphuric acid, and the gases evolved are passed into a measured quantity of a dilute solution of lead acetate. The colour of this solution is then compared with that obtained by treating a steel having a known amount of sulphur in a similar manner, and so on.

To estimate the manganese, the sample is dissolved in nitric acid, cooled, treated first with a small quantity of water, then with lead peroxide and a few drops of strong nitric acid, boiled for four minutes, and finally cooled. The manganese is calculated from the permanganate formed, which is estimated by comparing the colour with a standard as in the case of the sulphur. For phosphoric acid, the author prefers the molybdate method. D. A. L.

Estimation of Silicon in Iron and Steel. By T. Turner (*Chem. News*, **56**, 49—50).—It is shown by experiments that silicon can be correctly estimated in cast irons of very good quality by evaporation with dilute sulphuric acid; but with phosphoric irons the residues obtained are white but impure, and when in addition an iron contains titanium, the residue, although very nearly white, may have 20 per cent. of impurity, and contains iron, phosphoric acid, and titanium. Evaporation with sulphuric acid gives fairly good results with steels containing only a small quantity of silicon. In the aqua-regia method, the colour of the residue is usually an indication of its purity.

D. A. L.

Determination of Sulphur in Iron. By P. Platz (*Chem. Centr.*, 1887, 579).—The barium chloride method for the determination of sulphur in iron is modified as follows:—The iron and sulphur are oxidised by nitric acid; on prolonged boiling, the nitric acid is displaced by hydrochloric acid by gradually adding the latter. The whole is then evaporated until vapours of hydrogen chloride are no longer evolved, the residue diluted with water, and the insoluble silica filtered off. To the filtrate, barium chloride is added, and the precipitate collected and heated to oxidise any barium sulphide which may have been formed.

The precipitate is finally digested with hydrochloric acid to dissolve out the iron oxide, and weighed. Control experiments gave satisfactory results. V. H. V.

Volumetric Estimation of Cobalt in Presence of Nickel. By N. McCulloch (*Chem. News*, **56**, 27—29).—The author finds that cobalt "peroxide" is reduced by free iodine, iodides, hypochlorites, hypobromites, and hydrogen peroxide and ammonia to a lower oxide or oxides, possibly $Co_{13}O_{19}$, hence the author confirms Bayley's results (Abstr., 1879, 507), but he gives no hope of founding a method of estimating cobalt in presence of nickel, depending on the higher oxides of cobalt. D. A. L.

Separation of Nickel and Cobalt from Iron. By J. B. Macintosh (*Chem. News*, **56**, 64—65).—Proceeding at first by the old method of precipitating all three metals by ammonium sulphide, and treating with dilute hydrochloric acid; a solution with much iron and little nickel and cobalt, and a precipitate rich in nickel and cobalt but poor in iron are obtained. These are then treated separately in the ordinary way, by precipitating the iron as basic acetate, and perfect separation of the nickel and cobalt from iron is effected much more readily than by the "basic acetate" treatment alone.

D. A. L.

Direct Precipitation of Nickel Oxide in the Presence of Iron. By T. Moore (*Chem. News*, **56**, 3).—The solution containing the two metals, freed from acids, is treated first with glacial phosphoric acid or sodium pyrophosphate until the precipitate begins to dissolve, then with potassium cyanide which dissolves the remainder of the precipitate. This solution is now boiled for a couple of minutes, and the addition of potassium cyanide continued until potassium hydroxide does not give a precipitate. When cool, the solution is made alkaline with potassium hydroxide, excess of bromine solution in potassium hydroxide added, and the whole warmed; nickel and manganese (if present) are precipitated, iron and cobalt remain dissolved. The precipitate is dissolved in sulphuric acid and the nickel deposited electrolytically. Good results have been obtained with this method. D. A. L.

Water Analysis. (*Chem. News*, **56**, 113.)—The Chemical Section of the American Association for the Advancement of Science recommends the following plan for a uniform method of stating results of

water analysis. They are of opinion that two distinct schemes should be in use, one for mineral and one for potable waters. Mineral water results should state in parts per 1000, by weight, each basic element, each acid element in combination or supposed combination with the bases, the remaining acid elements being given in connection with all the oxygen of their salts (CO_3, SO_4, &c.). Volumes of gases expelled on boiling to be in cubic centimetres per litre. Constituents should be arranged in electropositive order, positive ones first. Potable water results to be stated in parts per million, to include—Total solids, chlorine, nitrogen expelled on boiling with sodium carbonate, and nitrogen as free ammonia, nitrogen expelled by boiling with alkaline permanganate and albuminoïd nitrogen, nitrogen as nitrite and as nitrate; organic matter; hardness. D. A. L.

Estimation of Methyl Alcohol in Presence of Ethyl Alcohol. By O. Hehner (*Analyst*, **12**, 25—29).—Since 1 part of ethyl alcohol (oxidised to acetic acid) reduces 4·278 parts of potassium dichromate, whilst 1 part of methyl alcohol requires 9·224 parts (oxidising to carbonic anhydride and water), the proportions of the two in a mixture can be calculated from a determination of the amount of dichromate reduced by 1 part of the mixture. This was confirmed by several experiments on mixtures of known composition. The oxidising solution contained 80 grams of dichromate, and 150 c.c. of concentrated sulphuric acid in the litre. Of the diluted alcohol, a quantity containing about 0·2 gram is mixed with 25 or 30 c.c. of the chromate solution in a bottle, which is corked and heated in boiling water for at least two hours. The unreduced chromate is then estimated by iron solution and standard dichromate. M. J. S.

Dimethyl Ethyl Carbinol. By B. Fischer (*Arch. Pharm.* [3], **25**, 777—779).—This compound (amylene hydrate) has recently been strongly recommended as an opiate. As it may be contaminated with fermentation amyl alcohol, which is poisonous, it should be subjected to the following tests. 1 gram is dissolved in 15 c.c. of water and tinted a faint red with permanganate solution; the colour ought not to change within 15 minutes (ethyl and amyl alcohol). 1 gram is dissolved in 15 c.c. of water, and slightly warmed with potassium dichromate and dilute sulphuric acid, no green colour should appear within half an hour (as above). 1 gram dissolved in 15 c.c. water is warmed with some drops of silver nitrate and a trace of ammonia. The silver should not be precipitated (aldehyde, with which most of the primary alcohols are contaminated). As an opiate this compound is more powerful than paraldehyde, but less so than chloral hydrate. Its therapeutic value depends on the fact that it affects neither the breathing nor the action of the heart. J. T.

Estimation of Glycerol in Fermented Liquids. By L. Legler (*Analyst*, **12**, 14—16).—The ordinary process, in which the crude glycerol is purified by extraction with ether-alcohol, is unsatisfactory, owing to the retention of some of the glycerol by the impurities. The author dilutes the crude glycerol with water, adds an excess of

potassium dichromate, and treats the mixture with sulphuric acid in a Will's carbonic acid apparatus in the ordinary way for a carbonic acid determination. Gentle boiling is required to complete the oxidation of the glycerol to carbonic anhydride and water. In analysing sweet wines, the glucose they contain may be destroyed by evaporation to dryness with baryta-water before extracting the glycerol with alcohol. Cane-sugar must first be inverted by boiling with hydrochloric acid. The crude glycerol contains impurities which yield carbonic anhydride on oxidation. The amount of these precipitated by ammoniacal solution of lead acetate is said to be constant and to be equivalent to 0·035 gram of glycerol per 100 c.c. of wine. Further experiments are promised. M. J. S.

Estimation of Glycerol and its Non-volatility with Aqueous Vapour. By O. Hehner (*Analyst*, **12**, 44—46, and 65—67).—The glycerol is oxidised as in Legler's process (preceding Abstract) by an excess of potassium dichromate and sulphuric acid, but the author measures the amount of dichromate reduced. One part of glycerol requires 7·486 parts of dichromate. The oxidising solution contains 80 grams of potassium dichromate, and 150 c.c. of strong sulphuric acid per litre. The unreduced excess is determined by titration with iron and standard dichromate. In moderately strong solutions (12 grams per litre), two hours' heating is sufficient to ensure the complete oxidation of the glycerol, but in highly dilute solutions a further addition of sulphuric acid is requisite. Such dilute solutions can, however, be concentrated by vigorous boiling without the loss of a trace of glycerol. Even a 50 per cent. solution boiled for two hours in a covered beaker, with continual replacement of the evaporated water (257 c.c.), did not suffer an appreciable loss of glycerol, whilst the loss from a 74 per cent. solution was very insignificant.

M. J. S.

Determination of Moisture in Starch. By F. W. Dafert (*Chem. Centr.*, 1887, 567).—Experiments are described to ascertain the temperature at which starch suffers the maximum loss in weight without appreciable decomposition. At 120° the loss was 11·31 per cent.; at 105—107°, 10·89 per cent.; and at 100° in a vacuum 11·9 per cent.; in the first case, the starch was slightly changed, but in the last it was unaltered. It is recommended that determinations of moisture should be conducted by this method. V. H. V.

Logwood Test for Alum in Bread. By W. C. Young (*Analyst*, **12**, 29—32, and 145—147).—Sour bread gives the same blue coloration with logwood as bread to which alum has been added. Specimens of bread which gave no indication with the logwood test, all showed the blue colour intensely after being moistened with very dilute acetic acid. Since aluminium phosphate is perceptibly soluble in cold, though not in hot, acetic acid, it is possible that this may account for the reaction after acidifying. M. J. S.

Estimation of Hydrocyanic Acid. By O. Linde (*Arch. Pharm.* [3], **25**, 690).—In the determination of hydrocyanic acid in bitter

almond water according to the Paris Pharmacopœia, the author proceeds as follows:—The bitter almond water is diluted with two volumes of water as the reactions then proceed most rapidly; basic magnesium acetate is added at once in considerable excess of the potassium chromate solution, not "some" drops, but only two drops per 27 grams of water to be added; of the silver solution almost sufficient to precipitate the whole of the acid should be added *at once;* the titration is best made by daylight, as the persistent red colour is not so well seen by gas- or lamp-light. J. T.

Estimation of Thiocyanic Acid. By P. Klason (*J. pr. Chem.* [2], **36**, 74—77).—If hydrochloric acid is not present, thiocyanic acid may be accurately determined by titration with silver nitrate. If hydrochloric acid is present the determination must be made by oxidation with permanganate. Here, however, the degree of concentration influences the result—which is always too low. If the concentration is not less than decinormal, the result is $1\frac{1}{2}$ per cent. too low, and this should be added to the amount found. L. T. T.

Estimation of Carbonic Acid in Beer. By C. A. Crampton and T. C. Trescot (*Amer. Chem. J.*, **9**, 290—293).—The cork of the bottle is pierced by a champagne tap and the gas passed through an Erlenmeyer's flask (to retain any foam), then dried by sulphuric acid and calcium chloride, and absorbed by soda-lime; the sample is afterwards heated to 80°, and the gas swept into the soda-lime tube by a current of pure air. The authors find an average of almost 0·4 per cent., most authorities giving an average of 0·1 to 0·2 per cent.; a higher amount of carbonic acid indicates either the addition of sodium bicarbonate or a state of after-fermentation. H. B.

Estimation of the Free Acid in Tannin Liquor by Titration. By R. Koch (*Dingl. polyt. J.*, **265**, 33—41).—In a previous communication (this vol., p. 871), the author recommended the use of albumin for the separation of tannin and the decolorisation of tannin liquor. He now finds that a solution of gelatin is preferable, as the precipitation of albumin by the aid of heat and the subsequent cooling is found to be inconvenient. It is necessary, however, to adjust the concentration of the gelatin solution to the amount of tannin in the liquor, otherwise difficulties in connection with the filtration and washing of the precipitate will arise. A solution containing 2 grams of gelatin in a litre of water is applicable to most liquors. The process is described in detail in the paper, and several test analyses are given. The author also states that powdered skin cannot be used for decolorising tannin liquor for the purpose of determining the free acid contained therein, owing to the fact that it absorbs acid from such liquors. D. B.

The Lactocrite; a New Apparatus for Determining Fat in Milk. By H. Faber (*Analyst*, **12**, 6—11).—The principle of this apparatus and method introduced by De Laval, consists in the separation of the fat by centrifugal force, after the caseïn has been

brought into such a condition that it does not prevent the union of the fat globules. This is effected by heating the milk with an equal volume of glacial acetic acid containing 5 per cent. by volume of concentrated sulphuric acid. The mixture is then introduced into a graduated tube, and several of these tubes at once are rotated for a few minutes in a specially constructed disc. The column of butter-fat obtained gives the percentage by a simple reading on the graduated tube. The results can be trusted to within 0·1 per cent. in whole milk, but in skimmed milk are about 0·2 per cent. too low.

M. J. S.

Reichert's Distillation Process. By A. H. Allen (*Analyst*, **12**, 11—13).—Porpoise oil and some samples of whale oil give nearly as large a percentage of volatile fatty acids as butter does. The appearance of solid fatty acids in the distillate is an indication of the presence of cocoanut oil. They should be filtered off before titrating. It is desirable to saponify the fat in a flask or closed bottle, since saponification in an open basin is found to give low results. The form of the distillation apparatus is of little importance. M. J. S.

Volumetric Estimation of Urea. By G. Campani (*Gazzetta*, **17**, 137—141).—The method described is based on the reaction of nitrous acid on urea, and estimation by alkalimetry of the carbonic anhydride evolved. In a tube of 150 to 200 c.c. capacity 20 c.c. of a 10 per cent. solution of potassium nitrite is introduced, then 2 c.c. of urine, and lastly 2 c.c. of 5 per cent. sulphuric acid. The tube is then fitted with a delivery tube, the contents gently warmed and the carbonic acid evolved is collected in lime-water of known strength. When the reaction is complete, the amount of lime neutralised by the carbonic anhydride is determined in the usual manner by a standard solution of oxalic acid; 1 mol. of carbonic anhydride corresponds with 1 mol. of urea, thus: $CO(NH_2)_2 + 2HNO_2 = 3H_2O + 2N_2 + CO_2$. The results obtained in test analyses are fairly concordant with one another and with those obtained by Liebig's method. It is necessary that the reaction should be allowed to proceed slowly; otherwise nitrous acid is evolved. V. H. V.

Estimation of Quinine Sulphate. By O. Hesse (*J. Pharm.* [5], **16**, 213—215).—1 gram of the sulphate dried at 100° is agitated with 20 c.c. of water at 60° and filtered after cooling; 5 grams of the filtrate is placed in a somewhat narrow test-tube; 2 c.c. of ether and five drops of ammonia are added; the tube is now stoppered and carefully agitated. The ethereal solution ought to be limpid, and should not deposit crystals. The author thinks that Paul's method gives good results when modified as follows: 5 grams of sulphate is dissolved in boiling water and allowed to crystallise; the mother-liquor is set aside and the crystals are dissolved in 120 c.c. of boiling water, recrystallised, and the process is repeated a third time, &c., the mother-liquor always being set apart. Three crystallisations suffice

with a salt containing 5 per cent. of cinchonidine sulphate; five crystallisations are indispensable when 9 per cent. is present. The mother-liquors of the three first crystallisations are evaporated to dryness, the residue is dissolved in dilute sulphuric acid, water is added to 20 c.c., and this is agitated with 16 c.c. ether and excess of ammonia. After 24 hours, the crystals of cinchonidine are collected. Similarly the remaining mother-liquors are made into a volume of 8 c.c., and treated with ammonia and 2 or 3 c.c. of ether; the crystals obtained are weighed with the preceding crop. The results thus obtained agree sensibly with those afforded by de Vrij's bisulphate method. J. T.

Testing Quinine Sulphate. By G. Kerner and A. Weller (*Arch. Pharm.* [3], **25**, 712—738, and 749—765).—The ammonia test for commercial quinine sulphate was proposed by one of the authors at a time when South America was the chief source of the salt, and the compound was almost free from cinchonidine; more recently Asiatic products have appeared in the market, in which cinchonidine often occurs in very considerable proportions. To meet the new conditions, the following method is proposed:—The sample of quinine sulphate is maintained at 40—50° until completely disintegrated, 2 grams in 20 grams of water is kept at 60—65° for half an hour with frequent stirring. The temperature is now brought to 15° and maintained at that for two hours with stirring, care being taken to have the temperature 15° exactly before the subsequent filtering. 5 c.c. of the filtrate is treated with ammonia of 0·96 sp. gr. until the precipitated quinine is again exactly dissolved. The amount of ammonia required should not exceed 10 c.c. The authors conclude that none of the methods hitherto proposed for the exact separation of cinchonidine and quinine are really exact. The same remark holds for the estimation of hydroquinine. J. T.

Detection of Hop-substitutes in Beer. By A. H. Allen (*Analyst*, **12**, 107—114).—A litre of the beer is evaporated to about 300 c.c. and precipitated hot with normal lead acetate, which is preferable to the basic or ammoniacal acetate of older processes. This throws down lupulin and hop-resin completely, leaving all or nearly all hop-substitutes in solution. After filtration, first hot and then cold, the lead is removed by hydrogen sulphide and the filtrate further concentrated. It is then acidified with sulphuric acid and shaken repeatedly with chloroform, which extracts absinthin, anthemin (chamomiles), quassiin, calumbin (colchicine, colocynthine, berberine, gentipicrin, picric acid, and picrotoxin imperfectly); ether is next employed to extract chiratin (chiretta), colocynthin, gentipicrin, picric acid, and picrotoxin. A further treatment with ether-chloroform after addition of ammonia completes the extraction of berberine and colchicine. If the residue from one of these solvents has a bitter taste, the presence of some hop-substitute is certain.

Quassiin, prepared by the above process, does not reduce Fehling's

solution or ammoniacal silver nitrate, and gives no coloration with strong sulphuric acid, or with nitric acid of 1·25 sp. gr., even on warming. It gives a mahogany-brown colour with ferric chloride. Its chloroform solution treated with an excess of bromine and then with ammonia gives a bright yellow colour (Christensen). A solution of 1 part of quassiin in 500,000 of water has a strong and persistent bitter taste. Gentipicrin and menyanthin reduce ammoniacal silver nitrate. With sulphuric acid, the former gives a red colour, the latter a yellowish-brown becoming violet-red on warming.

The chloroform extracts from chamomiles, calumba, colocynth, cocculus, and chiretta give no reaction with bromine and ammonia. The ether residue from chiretta, gives a straw-yellow colour changing to dull purplish-brown. Chiratin does not reduce Fehling's solution; it gives a copious precipitate with tannin. M. J. S.

Estimation of Ipecacuanha. By F. Ransom (*Pharm. J. Trans.* [3], **18**, 241—242).—The powdered ipecacuanha is thoroughly exhausted with chloroform that has been rendered alkaline by previous agitation with a strong solution of ammonia. An extraction apparatus is employed by means of which the exhaustion can be completed with hot chloroform. The solution is then agitated with dilute sulphuric acid, and the emetine in the acid solution estimated volumetrically by Mayer's reagent. R. R.

Detection of Aniline Colours in Wine, &c. By C. O. Curtman (*Zeit. anal. Chem.*, **26**, 555—556).—The formation of isonitriles when aniline-derivatives are warmed with potash and chloroform serves for the direct detection in wine of even minute traces of many of the aniline colours. The evolution of the isonitrile is accelerated by adding excess of strong sulphuric acid. M. J. S.

Estimation of Indigo. By G. Mannley (*Chem. Centr.*, 1887, 605).—In order to determine the proportion of indigo in a sample, the moisture is first estimated, and the dried mass introduced into a test-tube moistened with alcohol and a fine emulsion of grape-sugar in alcohol, and a few c.c. of soda solution added to it. The tube is then filled with alcohol, agitated for some time, left for 24 hours, and then poured into dilute sulphuric acid and oxidised by agitation. Hydrogen peroxide can also be used, and is to be preferred, because the precipitate in this case does not adhere so much to the walls of the vessel. The whole is allowed to remain for two days, filtered through a tared filter, dried and weighed. A gram of substance is a convenient quantity for the determination. V. H. V.

Testing Indigo Dyes on Fabrics. By W. Lenz (*Zeit. anal. Chem.*, **26**, 535—555).—In the course of an enquiry into the genuineness of the indigo dye on a certain fabric, an extensive examination of the methods of testing blue dyes was made, and those at present in use were found not to be altogether trustworthy. Stuffs were

dyed with 12 varieties of indigo, using dilute soda and zinc powder for the reduction in order to avoid the removal of impurities which takes place in the lime-copperas vat. In the case of one of the samples (fine Java indigo), the dyed fabric behaved with acidified alcohol as though it had received a second dyeing with logwood. This anomalous result appears to have been due to the formation of an unstable yellow product of the reduction of indigo. It could not be obtained again with the same sample.

For the detection of the more usual blue dyes the following methods may be trusted :—The stuff is warmed with an acidified 10 per cent. solution of stannous chloride. Prussian-blue remains unchanged. Indigo (vat-blue), indigo-carmine, cotton-blue (triphenylrosaniline trisulphonate) are completely removed from the fibres and yield pale-yellow solutions. Logwood is also removed but gives a rose-red solution. On adding a large excess of hydrogen peroxide to these solutions, the rose-red of logwood is destroyed, cotton-blue gives a blue solution, whilst indigo is not regenerated.

Glacial acetic acid, or concentrated formic acid, dissolves indigo from a fabric. In presence of logwood, either acid in the cold acquires a rose-red colour, which on heating passes into yellowish-red, and is soon obscured by the dissolving indigo. Prussian-blue is unaffected, and indigo-carmine is not dissolved if more than 48 hours have elapsed since the dyeing. On mixing the acetic acid solution with ether and then adding water until the ether separates, the indigo is removed from the aqueous layer, which then in the presence of logwood shows a feeble reddish-yellow tint. If now a few drops of concentrated hydrochloric acid is added, the smallest trace of logwood is revealed by the production of a rich red colour in the aqueous layer. Cotton-blue obscures this reaction. In this case, the aqueous layer must be separated and shaken with chloroform, or better amyl alcohol, which abstracts the aniline-blue. Another method of examining the acetic acid solution is to mix 1 c.c. of it with 5 c.c. of chloroform, then add 2 c.c. of water and crystallised sodium carbonate until alkaline. The chloroform layer is then separated and shaken with strong borax solution, which frees it from logwood. It is then mixed with ether and dilute acetic acid, when the aniline blue passes into the acid and the indigo remains in the mixture of ether and chloroform. The alkaline solution contains the indigo-carmine and logwood; this is acidified with acetic acid and shaken with amyl alcohol, which removes the logwood with reddish colour, further intensified by hydrochloric acid.

If a fabric dyed with the above colours is boiled with borax solution the logwood-blue and indigo-carmine are dissolved, whilst Prussian-blue is decomposed. Aniline-blue and vat-blue remain on the fibre, and may be distinguished by warming with ferric chloride. The filtered borax solution, which in presence of indigo-carmine is blue, is tested for logwood by stannous chloride.

As a special test for logwood, the stuff may be treated directly with hydrochloric acid, or boiled with a 10 per cent. solution of alum, or of glucinum chloride to which an excess of ammonium carbonate is subsequently added. Ammonium molybdate gives at once an intense

blue-violet. The absorption spectra of many of these solutions are figured.

A fabric dyed with indigo alone should stand the following tests: —Alcohol should dissolve no colour even on gentle warming; cold saturated oxalic acid and borax solutions, 10 per cent. alum solution, and 33 per cent. ammonium molybdate must remove no colour even on boiling. Stannous or ferric chloride destroys the colour on warming. Glacial acetic acid dissolves all the colour on repeated boiling, and after mixing the solution with ether and water the aqueous layer is colourless and is not coloured by strong hydrochloric acid. The fabric boiled with hydrochloric acid evolves no hydrogen sulphide, and the acid extract warmed with a large excess of alkali and some chloroform evolves no odour of isonitriles. M. J. S.

Detection of Artificial Colouring Matters in Butter, &c. By E. W. Martin (*Analyst*, **12**, 70).—The following method serves for the detection of annatto, turmeric, carotin, and the aniline- and naphthol-yellows. Two parts of carbon bisulphide are gradually added to 15 parts of methyl alcohol, with gentle shaking; to 25 c.c. of the mixture, in a convenient tube, 5 grams of the butter-fat or oil is added, and the tube is shaken. In a few minutes the bisulphide falls to the bottom, carrying with it the fat, whilst the foreign colouring matter remains in the alcohol. The natural colouring matters of fats, &c., do not colour the methyl alcohol. M. J. S.

Pettenkofer's Reaction. By F. Mylius (*Zeit. physiol. Chem.*, **11**, 492—496).—The cause of the blood-red colour produced on adding cane-sugar and sulphuric acid to cholic acid (Pettenkofer's reaction) is unknown. The same colour is produced by the bile acids, by choleïc acid, and by the distillation products of cholic acid. On the other hand, dehydrocholic acid and bilianic acid do not give it; in these latter acids hydroxyl is absent, and it is not improbable that the reaction depends on the presence of the hydroxyl-group. The reaction may be obtained by using furfuraldehyde instead of sugar. That it is not the sugar itself on which the reaction depends, but some volatile substance, was considered probable, because the reaction was obtained from the distillate of sugar with dilute sulphuric acid; acetone, mesityl oxide, and phorone, which are formed in this process, do not give the reaction, but furfuraldehyde, which is also formed, does. As a test for furfuraldehyde, it is exceedingly delicate, a drop of a mixture of water and furfuraldehyde in the proportion 20,000 to 1 gives the colour on the addition of cholic acid and sulphuric acid; in other words, the fortieth part of a milligram can be thus detected. The colour can be extracted by ether, which is coloured blue by it.

Other substances, however, besides cholic acid give the same reaction with furfuraldehyde, namely, isopropyl alcohol (to a slight extent), isobutyl alcohol (very intensely), allyl alcohol, trimethyl carbinol, dimethyl ethyl carbinol, amyl alcohol, oleïc acid, and petro-

leum. Among the substances which do not give the colour are the following:—Ethyl alcohol, propyl alcohol, capryl alcohol, acetic acid, isobutyric acid, acraldehyde, and benzene. The substances which give the test are seen in general to be unsaturated compounds, or those which by the loss of water become unsaturated; it is considered not improbable that the reaction depends on some hydrocarbon produced from the foregoing compounds when they lose water owing to the action of sulphuric acid. W. D. H.

Detection of Albumin in Urine. By A. Liebermann (*Chem. Centr.*, 1887, 600).—If albumin is extracted a few times with alcohol, and then washed with cold ether, it gives a deep violet coloration if heated with concentrated hydrochloric acid (sp. gr. 1·196). Positive results were obtained with various pathological products, but experiments with hæmoglobulin, chondrin, and keratin, were unsuccessful. In the case of urine, the liquid is at first boiled with a small quantity of acetic acid, and the precipitated albumin treated as above; the reaction succeeded with 5 c.c. of urine to which 0·1 per cent. of egg-albumin was added. V. H. V.

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ERRATA.

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Page	Line				
30	18	from top,	*for*	"α-β-dimethylglycidic acid"	*read* "α-β-dimethylglyceric acid."
55	16	,, bottom,	,,	"paratoluene-β-naphthol"	,, "paratoluene-azo-β-naphthol."
122	20	,, ,,	,,	"Mansfield"	*read* "Mansfeld."
239	4	,, ,,	,,	"β-methylacetopentathiënone"	*read* "β-methylpentathiënone."
306	14	,, top,	,,	"Bunsen-pump"	*read* "water-pump."
327	12	,, bottom,	,,	"no ozone is produced,"	*read* "ozone is produced in large quantities."
446	6	,, ,,	,,	"$SnCl_2,2PbO,5H_2O$,"	*read* "$SrCl_2,2PbO,5H_2O$."
461	20 & 31	,, top,	,,	"diisobutyl,"	,, "diisobutylamine."
472	3	,, ,,	,,	"Methyl bromisopropyl oxide,"	*read* "Methyl bromisopropylphenyl oxide."
475	6	,, ,,	,,	"melts"	*read* "boils."
516	21	,, ,,	,,	"Lawes, Gilbert and Warington,"	*read* "Lawes and Gilbert."
561	21	,, bottom,	,,	"Pseudomorphite,"	*read* "Pseudophite."
581	15	,, ,,	,,	"paratolylcarbimide,"	*read* "paratolylthiocarbimide."
607	12	,, top,	,,	"adheres to the statement he previously made, that cholic acid does not give an acetyl compound,"	*read* "finds that the product of the action of acetic anhydride on cholic acid yields an acetate when boiled with alcoholic potash."
675	6	,, ,,	,,	"β-naphthalthiamide,"	*read* "β-naphthylthiamide."
721	11	,, ,,	,,	"phenyl,"	*read* "phenol."
732	11	,, ,,	,,	"Paradiazoazoimide,"	*read* "Paradiazoazotoluenimide."
774	3	,, bottom,	,,	"B. Claassen,"	*read* "E. Claassen."
798	22	,, ,,	,,	"Fredrich,"	,, "Friedreich."
840	11 & 15	,, top,	,,	"α"	*read* "β."
879	5	,, bottom,	,,	"$\left[\log\frac{pw}{p}\right]=\left[\log\frac{pw}{p}\right]_{T_1}+\frac{s}{RA}\int_{T_1}^{T_1}V\frac{dT}{T^2}$,"	*read* "$\left[\log\frac{pw}{p}\right]_T=\left[\log\frac{pw}{p}\right]_{T_1}+\frac{s}{RA}\int_{T}^{T_1}V\frac{dT}{T^2}$."
880	15	,, top	,,	"$f-t\left(\frac{df}{dt}\right)_v c/v^2$,"	*read* "$f-t\left(\frac{df}{dt}\right)_v=c/v^2$."
880 to 882	10 to 24 / 5 / 10	,, ,, / ,, bottom, / ,, top,		Mutually transpose paragraphs:— "The present research . . . . . unless the value of *a* be altered:" and "Put $x=$ . . . . . in several cases."	
881	20	,, ,,	*for*	"$dv-d(pv)$"	*read* "$dv+d(pv)$."
887	9	,, bottom,	,,	"100°"	,, "−100°."
888	12	,, top	,,	"**204**"	,, "**240.**"
923	3	,, ,,	*delete*	"alkyl."	
992	24	,, ,,	*for*	"produce"	,, "produced."
,,	7	,, bottom,	,,	"found"	,, "ground."
993	10	,, ,,	,,	"16 grams"	,, "260 grams."
996	23	,, top	,,	"Pumphuston"	,, "Pumpherston."
1047	21	,, bottom,	,,	"Glycosuric acid contains neither oxygen nor nitrogen,"	*read* "Glycosuric acid contains oxygen but not nitrogen."
1086	12	,, top	,,	"Shaelinger,"	*read* "Schelinger."
1128	16	,, ,,	,,	"Wayl,"	,, "Weyl."
1150	9	,, ,,	,,	"A. Liebermann,"	*read* "L. Liebermann."

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